Effects of Electron Exchange on the Photochemical, Electrochemical and Electrocatalytic Responses of Polymer Modified Electrodes

Thesis by

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To my wife, Kathie,
and to my parents.

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Special thanks are due Elaine Williams for her expert typing.

Abstract

A spectroelectrochemical method is presented which may be used to measure the concentrations of the two oxidation states of a redox couple in a polymer film. The method is applied to $Ru(bpy)_3^{2+}$ in Nafion films on transparent tin oxide electrodes. Measurements of the emission of this complex in Nafion films on graphite and tin oxide electrodes are used to obtain information about the quenching of $Ru(bpy)_3^{2+*}$ by $Ru(bpy)_3^{3+}$. Features of the luminescence which yield insight into the structure of the Nafion film are discussed.

Experiments are described which bear on the question of when electron self-exchange reactions can contribute to the propagation of electrons through polymer films on electrodes. The results of experiments on the $Co(bpy)_3^{2+/+}$ couple are discussed in terms of a theory derived by Dahms and Ruff et al. which describes the contribution of electron self-exchange reactions to diffusion in mixtures containing both halves of a redox couple.

The propagation of charge through polymer films by electron exchange cross-reactions between different redox couples which are co-incorporated into a polymer film on an electrode is discussed. Two experimental examples of this phenomenon are presented.

An electrocatalytic application of a polymer modified electrode is described. Cobalt tetraphenylporphyrin is incorporated into a Nafion film on a graphite electrode, and this porphyrin is

used to catalyze the two-electron electroreduction of dioxygen. Enhanced catalytic currents are observed when an electron mediator ($Ru(NH_3)_6^{3+}$) is added to the film. This mediator serves to shuttle electrons between the electrode and the relatively immobile catalyst sites. The performance of electrocatalysts in polymer films is discussed with emphasis on ways to enhance stability without sacrificing efficiency.

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CHAPTER I

INTRODUCTION

In the ten years following the pioneering work of Lane and Hubbard[1] the study of the deliberate modification of electrode surfaces has grown increasingly popular. A major reason for the intense interest in this new field is the expectation that the ability to vary the chemical nature of the electrode surface will give the electrochemist unprecedented control over the rates and selectivities of redox processes which occur there. This is possible because the immobilization of different species on electrodes should bestow the chemical and physical properties of these species on the electrode surface. For example, by choosing as the surface modifying agents redox species which are known to catalyze certain types of reactions, this same reactivity may be imparted to the electrode. Applications in which the modification of electrode properties would be advantageous include electrocatalysis,[2] inhibition of photocorrosion at semiconductor electrodes,[3] electrochromic devices[4] and others. In pursuit of these goals, many different electrodes have been combined with different surface modifying agents to yield a wide variety of modified electrodes. Several reviews[5-7] have been published describing recent developments in the field. This discussion will be concerned only with polymers as modifying agents and, in particular, with the manifestations of electron exchange processes in polymer modified electrodes.

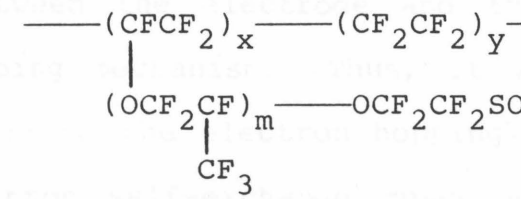
A polymer modified electrode is simply an electrode which has had a polymer attached in some way to its surface. This attachment may occur by physical adsorption of the polymer on the electrode surface[8] or by the creation of chemical bonds between functional groups present on the electrode surface and on the polymer.[9] For the case of physical adsorption, the immobilization of the polymer at the electrode surface may result from interactions between the polymer and the electrode and/or from the relative insolubility of the polymer in the chosen solvent. Thus, in many cases, the experimental conditions must be carefully chosen in order to obtain a polymer film with the desired characteristics. Common methods of preparing polymer modified electrodes based on physical adsorption include application of an aliquot of a polymer solution onto the electrode surface followed by evaporation of the solvent,[10] spin-coating,[11] and electropolymerization,[12] in which the polymerization is carried out at the electrode surface after initiation by an electrochemical reaction.

There are two general classes of polymer modified electrodes, those in which the redox species are covalently bonded to the polymer[13] and those in which the redox species are incorporated into coatings of polymers bearing charged ionic groups. This process is termed electrostatic binding[14] and is based on the phenomenon of ion-exchange. Each of these classes has its own virtues and handicaps. The former class suffers from a lack of generality because rather involved synthetic procedures are

required, however, the polymer films obtained tend to be very stable. The latter class enjoys the advantages of simplicity and generality, but because of the reversible nature of the incorporation process the redox species may be easily lost. All of the work described in this Thesis was done with polymer modified electrodes of the latter class, so the discussion will be largely limited to their properties.

Oyama and Anson[14] first demonstrated that if electrodes are coated with polymers having charged ionic groups (such as protonated polyvinylpyridine), the resulting polymer films incorporate ions of the opposite charge (such as $IrCl_6^{2-}$) from aqueous solutions. In the case that these incorporated ions undergo redox reactions, their electrochemical response is generally observed at or near the potential at which it would be observed in solution. It was also shown that the response of these incorporated ions persists for some time even after the coated electrode has been transferred to a solution which does not contain the redox ion. In the initial studies[14,15] of electrostatic binding of redox species in polymer films on electrodes, the polymers which were used were either positively charged or negatively charged so as to incorporate anionic or cationic transition metal complexes, respectively. The stabilities of the films cast using cationic polymers were found to be generally good, while the stabilities of the anionic polymer films were quite poor. This is probably due to dissolution of the anionic polymers from the electrode surface.[15]

However, in 1980, Rubinstein and Bard[16] reported that Nafion,[17] a perfluorinated, sulfonate-based ion-exchange polymer with the structure shown below,



could be used to prepare films on electrodes which resisted dissolution in aqueous solutions. Thus, with the availability of stable films of polymers having either anionic or cationic charged groups, the electrostatic binding method began to show promise of general applicability for the incorporation of a wide variety of charged redox species.

The early experiments on polymers containing electrostatically bound redox species revealed that electrochemistry could be observed from the equivalent of many monolayers of the incorporated ions.[14,15] The mechanism by which the species which are distant from the electrode surface become oxidized or reduced is of considerable interest. Kaufman and Engler[18] originally proposed that electrons could propagate through polymer films containing covalently attached redox species by hopping from one species to the next. In films of this type which contain the equivalent of many monolayers of electroactive redox species it is difficult to imagine any other reasonable mechanism for charge propagation. However, in films containing electrostatically bound redox ions there are at least two possible mechanisms for

this process. The redox ions may undergo molecular diffusion from points within the bulk of the polymer film to the electrode surface in order to be oxidized or reduced, and the electrons may propagate between the electrode and the redox ions by the electron hopping mechanism. Thus, it is expected that under certain conditions the electron hopping mechanism, which results from an electron self-exchange reaction, will contribute to charge propagation, while in others it will not.

These and other considerations provoked a number of studies designed to investigate how the incorporation of redox ions into charged polymer films affects their electrochemical responses, and especially how these responses are affected by electron exchange processes. This Thesis describes a series of such studies on Nafion coated electrodes.

In Chapter II[19] a spectroelectrochemical method is presented which may be used to measure the concentrations of the two oxidation states of a redox couple in a polymer film so as to determine whether or not the response of the couple to the electrode potential is Nernstian. Measurements of the emission of an electroactive, luminescent redox ion in the Nafion film are used to obtain information about the quenching of the luminescence of one half of the redox couple by the other half of the same couple. Features of the luminescence which yield insight into the structure of the Nafion film are discussed.

Chapter III[20,21] describes experiments which bear on the question of whether electron self-exchange reactions can contribute to the propagation of electrons through polymer films on electrodes. The experimental results are discussed in terms of a theory derived by Dahms[22] and Ruff and Friedrich[23] which describes the contribution of electron self-exchange reactions to diffusion in mixtures containing both halves of a redox couple.

The propagation of charge through polymer films by electron exchange cross-reactions between different redox couples which are co-incorporated into a polymer film on an electrode is discussed in Chapter IV. Two experimental examples of this phenomenon are presented.

Chapter V describes an electrocatalytic application of a polymer modified electrode. A cobalt porphyrin is incorporated into a Nafion film on a graphite electrode, and this porphyrin is used to catalyze the two-electron electroreduction of dioxygen. Enhanced catalytic currents are observed when an electron mediator is added to the film. This mediator serves to shuttle electrons between the electrode and the porphyrin molecules which are not in electronic contact with the electrode. The performance of electrocatalysts in polymer films is discussed with emphasis on ways to enhance stability without sacrificing efficiency.

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CHAPTER II

Electrochemical Control of the Luminescent Lifetime of $Ru(bpy)_3^{2+*}$ Incorporated in Nafion Films on Graphite Electrodes

INTRODUCTION

The increasing popularity of polyelectrolyte coatings as matrices for binding redox complexes to the surfaces of electrodes[1-8] has enhanced the need for studies of the effects of the polyelectrolyte environment on the thermodynamic properties and kinetic behavior of the incorporated redox reagents. Rubinstein and Bard[5,6] recently described the use of polyanion films of Nafion[9] to bind $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) to the surface of pyrolytic graphite, glassy carbon, and Pt electrodes to study the chemiluminescence of $Ru(bpy)_3^{2+*}$ that was electrogenerated by oxidizing $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ in the presence of oxalate ions. The time and potential dependence of the luminescence could be accounted for by either of two alternative mechanisms that were difficult to choose between on the basis of the data obtained.[6]

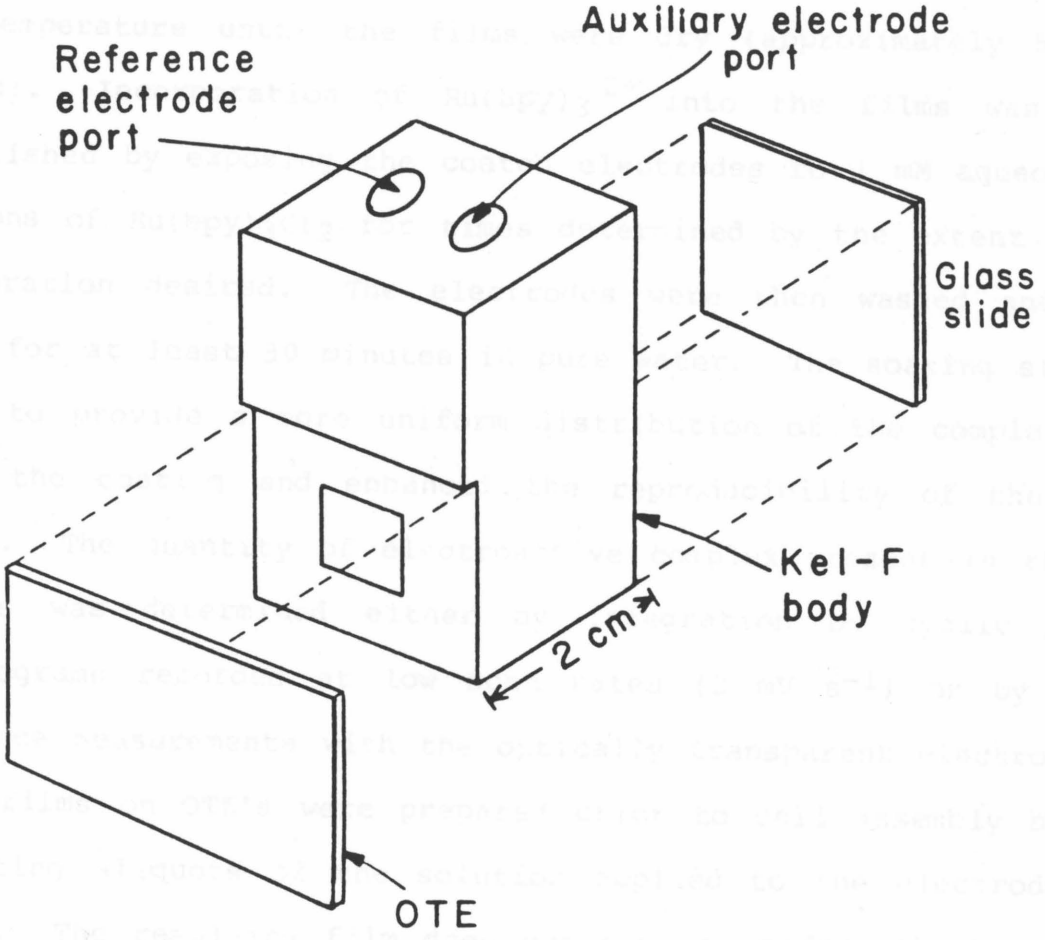
The present work describes an investigation of the properties of cationic redox complexes electrostatically bound in Nafion films. By measuring the lifetime of photogenerated $Ru(bpy)_3^{2+*}$ ions in Nafion coatings on graphite electrodes as a function of the electrode potential it has been possible to measure the rate

at which $Ru(bpy)_3^{3+}$ quenches $Ru(bpy)_3^{2+*}$ within the polyelectrolyte film. The results point to the likely mechanisms by which $Ru(bpy)_3^{2+*}$ was generated in the experiments of Rubinstein and Bard[6] as well as providing information on the internal structure of Nafion films cast on graphite electrodes.

EXPERIMENTAL

Materials. A 5.2 wt.% solution of relatively low molecular weight Nafion (in the sulfonic acid form) in a 5/1 mixture of isopropanol/water was available from a sample supplied by E. I. du Pont de Nemours Company a number of years ago. Commercially available $Ru(bpy)_3Cl_2$ (G. F. Smith Chem. Co.) and $Ru(NH_3)_6Cl_3$ (Matthèy Bishop, Inc.) were recrystallized from water prior to use. Basal plane pyrolytic graphite (BPG) electrodes (Union Carbide Co.) were cut and mounted as previously described.[10] The antimony-doped tin oxide optically transparent electrodes (OTE) were available in these laboratories. The electrochemical cell used in the emission experiments with the BPG electrodes was a standard 1 cm. emission cell joined at the top to a reference compartment. The cell used in the spectroelectrochemical and lifetime measurements, shown in Fig. 2.1, was fabricated from a block of Kel-F. A hole was cut through the center of the block and a glass microscope slide was glued to one side of the block and the OTE to the other to form a watertight compartment. The glue was type S-804 epoxy (Saunders Corp.). The reference and auxiliary electrodes were introduced into the cell through two holes drilled through the top. The connection to the OTE was made by clamping an electrical connector directly to the electrode. The reference electrode was Ag/AgCl(KCl, sat.) with respect to which all potentials are quoted. The supporting electrolyte was 0.1 M CF_3COOH - 0.1 M CF_3COONa.

Figure. 2.1 Exploded view of the Kel-F cell used in the spectroelectrochemical (Nernst plot) and lifetime measurements.


Auxiliary electrode port
Reference electrode port
Glass slide
Kel-F body
2 cm
OTE

Procedures and Instrumentation. Nafion films on graphite electrodes were prepared by carefully syringing microliter amounts of the 5.2 wt.% stock solution onto a freshly cleaved electrode, making sure that the polymer solution completely covered the surface. The solvent was allowed to evaporate at room temperature until the films were dry (approximately 5 minutes). Incorporation of $Ru(bpy)_3^{2+}$ into the films was accomplished by exposing the coated electrodes to 1 mM aqueous solutions of $Ru(bpy)_3Cl_2$ for times determined by the extent of incorporation desired. The electrodes were then washed and soaked for at least 30 minutes in pure water. The soaking step helped to provide a more uniform distribution of the complex within the coating and enhanced the reproducibility of the results. The quantity of electroactive complex present in the coatings was determined either by integration of cyclic voltammograms recorded at low scan rates (2 mV s^{-1}) or by absorbance measurements with the optically transparent electrode. Nafion films on OTE's were prepared prior to cell assembly by evaporating aliquots of the solution applied to the electrode surface. The resulting film does not have a uniform thickness. The outer quarter of the film is about 3 to 5 times thicker than its central portion.[11,12] Much of the $Ru(bpy)_3^{2+}$ that enters this thicker portion of the film is not in electronic contact with the underlying electrode and is thus electro-inactive. This becomes clearly evident if the electrode potential is adjusted to 1.3 volt where all of the electroactive complexes in the film are

oxidized to $Ru(bpy)_3^{3+}$ which shows no luminescence under irradiation. Illumination of such oxidized films with blue light produces a bright orange emission from the outer, thicker portion of the film with none from the central portion.

In order to obtain films of more uniform thickness the outermost quarter of each film was carefully removed with a scalpel before the electrode was mounted. Thicknesses of the coatings were monitored with a Dektak Profilometer (Sloan Co.). The coated electrode was glued to the Kel-F cell and placed in an oven at 100°C for 10 minutes to set the glue. $Ru(bpy)_3^{2+}$ was incorporated in the coating by filling the cell with a 1 mM solution of the complex and allowing incorporation to proceed until the desired quantity of complex had entered the film. Electrochemical measurements were conducted with a Princeton Applied Research (PAR) 173 potentiostat driven by a PAR 175 universal programmer. The luminescence measurements employed a Perkin-Elmer Model MPF-3 emission spectrophotometer or a locally constructed instrument with a tungsten light source.[13] For spectroelectrochemical measurements the Kel-F cell was mounted in a Hewlett-Packard Model 8450A spectrophotometer.

Emission lifetimes were measured by the following procedure: The absorbance of the Nafion-$Ru(bpy)_3^{2+}$ coating on an OTE mounted in the spectroelectrochemical cell was monitored spectrophotometrically while the electrode was adjusted to each potential of interest. The absorbance changes accompanying each change in potential were usually complete within 60 seconds but the

electrode was held at each potential for 20 additional minutes to assure uniformity of the concentrations of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ in the films. The cell was then disconnected from the potentiostat and quickly transferred to a computer-controlled pulsed laser apparatus to be described.[14] Spectral monitoring of the coating after the approximately 2 minutes required for the transfer showed that none of the $Ru(bpy)_3^{3+}$ was reduced by reaction with H_2O in the acidic electrolytes employed. The coated electrode was irradiated with 8 nsec pulses of 532 nm radiation that was filtered so as to deliver ca. 1 mJ of energy per pulse. The temporal decay of the resulting luminescence in the coating was monitored, and the lifetime of the emitting complex was computed by fitting the data to a simple exponential function.[14]

RESULTS

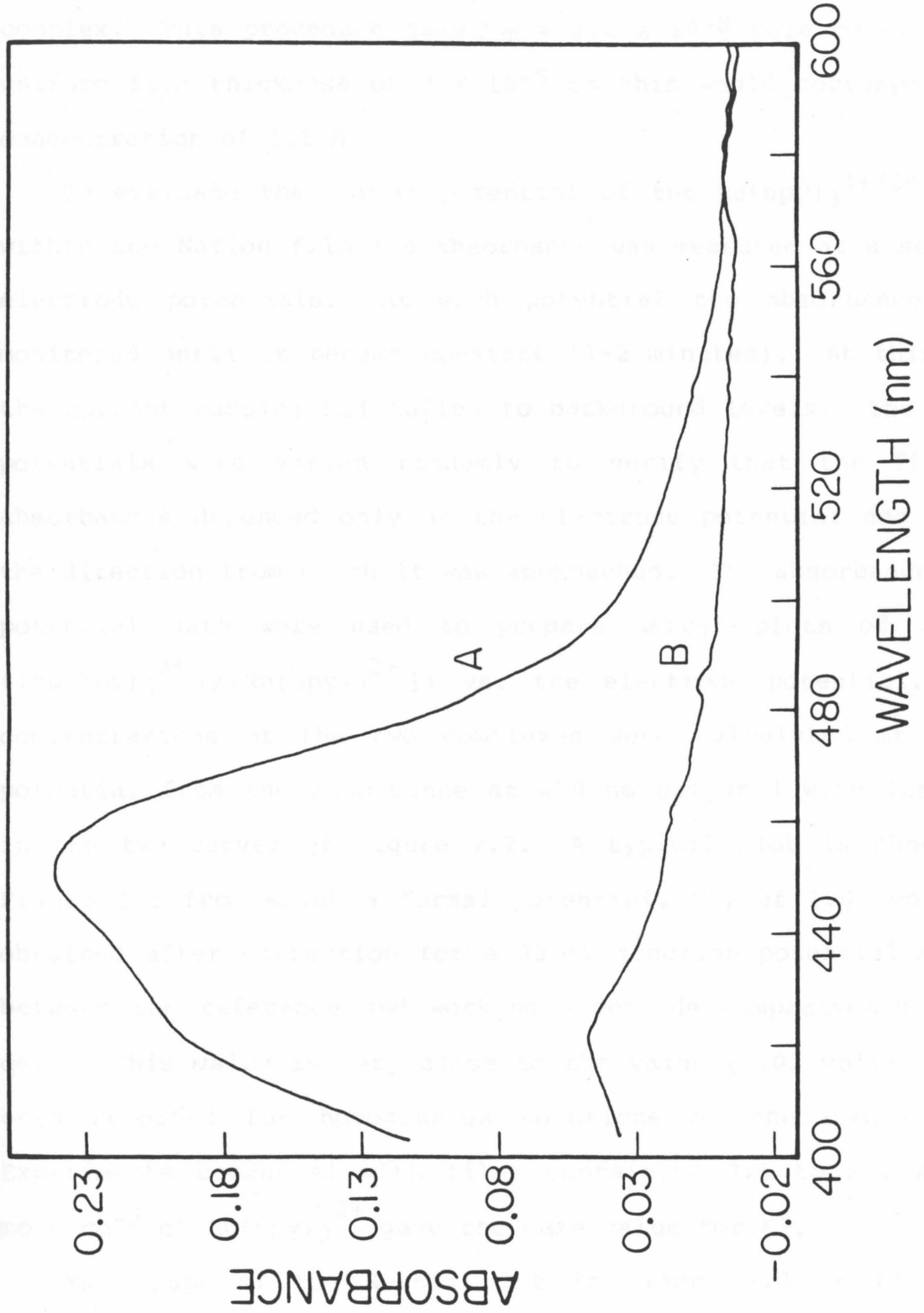
Spectroelectrochemistry on Tin Oxide Electrodes. Curve A in Figure 2.2 is the spectrum of $Ru(bpy)_3^{2+}$ incorporated in a Nafion film approximately 2 X 10^{-5} cm thick deposited on a transparent tin oxide electrode immersed in a supporting electrolyte solution (0.1 M CF_3COOH - 0.1 M CF_3COONa). Curve B is the spectrum that resulted when the electrode was held at 1.3 volt for 10 minutes to oxidize the incorporated complex to $Ru(bpy)_3^{3+}$. Separate experiments in solution showed that the molar absorptivity of $Ru(bpy)_3^{3+}$ at 450 nm is 4% that of $Ru(bpy)_3^{2+}$, so the two spectra in Figure 2.2 show that over 95% of the $Ru(bpy)_3^{2+}$ incorporated by the film is susceptible to electro-oxidation. The total cross-sectional concentration of the electroactive complex in the film, Γ_T, was evaluated from the difference in absorbances at 450 nm for the two spectra in Figure 2.2, ΔA, and the molar absorptivity of $Ru(bpy)_3^{2+}$, ε_{450}, according to equation (2.1)

$$\Gamma_T = \Delta A/\varepsilon_{450} \qquad (2.1)$$

which is valid so long as the diameter of the transmitted light beam is smaller than that of the film whose absorbance is being measured. The value of ε_{450} was set equal to its value in homogeneous solutions of $Ru(bpy)_3^{2+}$ (ε_{450} = 1.46 X 10^4 [15] because curve A in Figure 2.2 exhibits no features that distinguish it from the spectrum recorded with a homogeneous solution of the

Figure 2.2 (A) Absorption spectrum of $Ru(bpy)_3^{2+}$ incorporated in a Nafion film on a transparent tin oxide electrode. The average film thickness was 2×10^{-5} cm and 2.2×10^{-8} mole cm^{-2} of complex were incorporated in it.

(B) Absorption spectrum of the film after the electrode potential was held at 1.3 volt for 10 minutes. Supporting electrolyte: 0.1 M CF_3COOH - 0.1 M CF_3COONa.

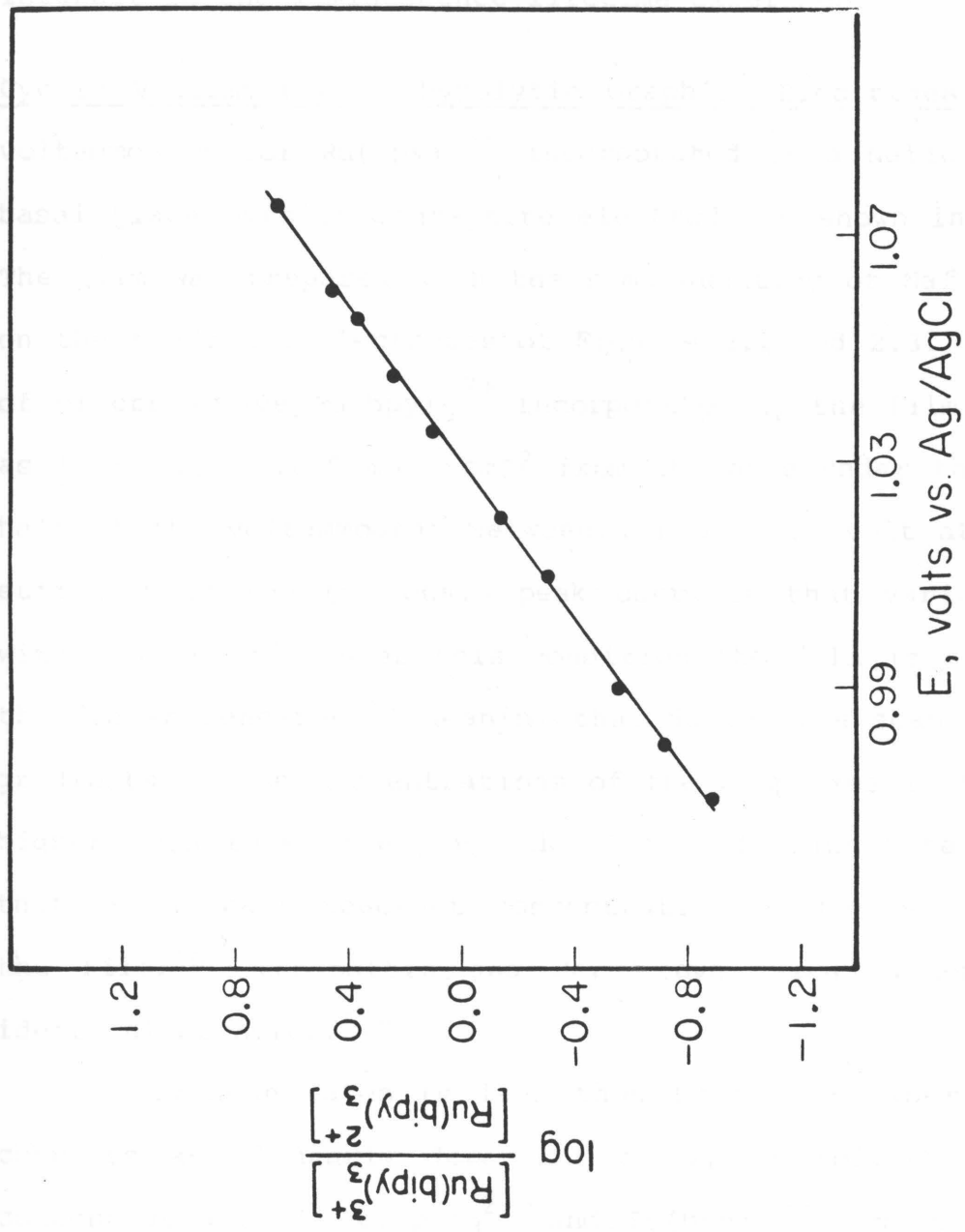

ABSORBANCE
0.23
0.18
0.13
0.08
0.03
-0.02
400
440
480
520
560
600
WAVELENGTH (nm)
A
B

complex. This procedure gave Γ_T = 2.2 X 10^{-8} mole cm^{-2}. For a uniform film thickness of 2 X 10^{-5} cm this would correspond to a concentration of 1.1 M.

To evaluate the formal potential of the $Ru(bpy)_3^{3+/2+}$ couple within the Nafion film its absorbance was measured at a series of electrode potentials. At each potential the absorbance was monitored until it became constant (1-2 minutes). At this point the current passing had fallen to background levels. The applied potentials were varied randomly to verify that the final absorbances depended only on the electrode potential and not on the direction from which it was approached. The absorbance-potential data were used to prepare Nernst plots of log ($[Ru(bpy)_3^{3+}]/[Ru(bpy)_3^{2+}]$) vs. the electrode potential. The concentrations of the two complexes were calculated at each potential from the absorbance at 450 nm compared with its value in the two curves of Figure 2.2. A typical plot is shown in Figure 2.3 from which a formal potential, E^f, of 1.03 volt was obtained after correction for a 30 mV junction potential measured between the reference and working electrode compartments in the cell. This value is very close to the value (1.02 volt) that has been reported for homogeneous solutions of the complex.[15] Experiments conducted with films containing 0.5 to 2.2 X 10^{-8} mole cm^{-2} of $Ru(bpy)_3^{2+}$ gave the same value for E^f.

The slope of the Nernst plot in Figure 2.3 is 70 mV, significantly larger than the 59 mV expected for an ideal redox couple. This difference is not unexpected considering the large

Figure 2.3 Nernst plot for the $Ru(bpy)_3^{3+/2+}$ couple incorporated in the Nafion film of Figure 2.2.

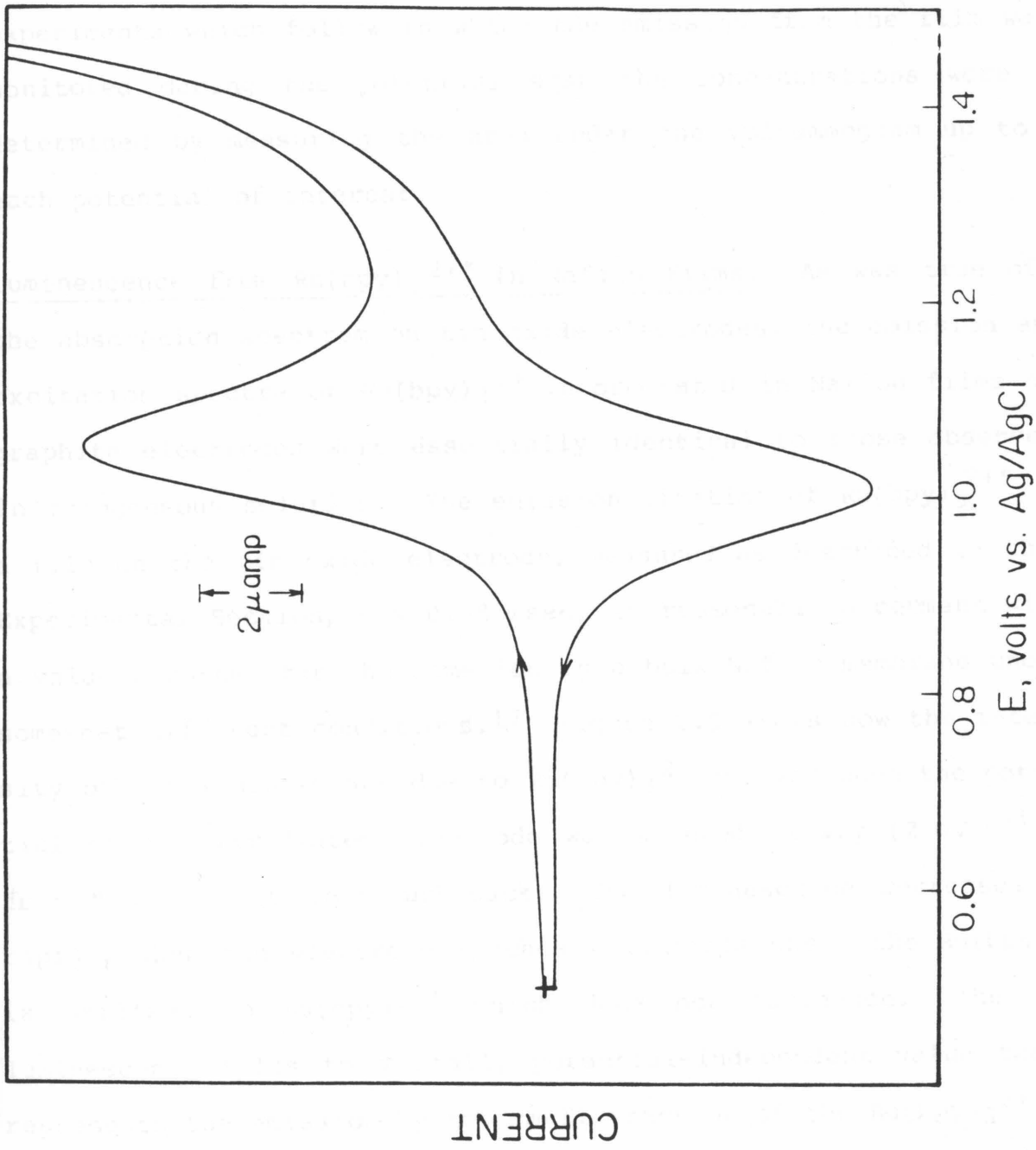

1.2
0.8
0.4
0.0
−0.4
−0.8
−1.2
log [Ru(bipy)3 3+] / [Ru(bipy)3 2+]
0.99
1.03
1.07
E, volts vs. Ag/AgCl

effective concentration (1.1 M) of the highly charged reactants. Fortunately, the non-ideal behavior did not destroy the linearity of the Nernst plots which were used to evaluate the concentrations of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ at each electrode potential of interest in the luminescence lifetime experiments.

Cyclic Voltammetry on Pyrolytic Graphite Electrodes. A cyclic voltammogram for $Ru(bpy)_3^{2+}$ incorporated in a Nafion film on a basal plane pyrolytic graphite electrode is shown in Figure 2.4. The film was prepared with the same quantity of Nafion as those on the tin oxide electrodes of Figures 2.2 and 2.3. The quantity of electroactive $Ru(bpy)_3^{2+}$ incorporated by the film was measured as $\Gamma_T = 2.5 \times 10^{-8}$ mole cm^{-2} from the area under the reductive half of the voltammogram between 1.1 and 0.7 volt at scan rates sufficiently low to obtain peak currents that varied linearly with scan rate. Under this condition the film is said to have thin-layer behavior,[16] meaning that during the scan there are no gradients in the concentrations of the complexes in the film. At higher scan rates the waves develop "diffusional tails" showing that significant reactant concentration gradients exist within the film.[16] Rubinstein and Bard have reported essentially identical behavior.[5,6]

At low scan rates (v less than 10 mV s^{-1}) where the peak currents are linearly dependent on v, it follows that the concentrations of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ remain essentially uniform throughout the film during the potential scan. This is

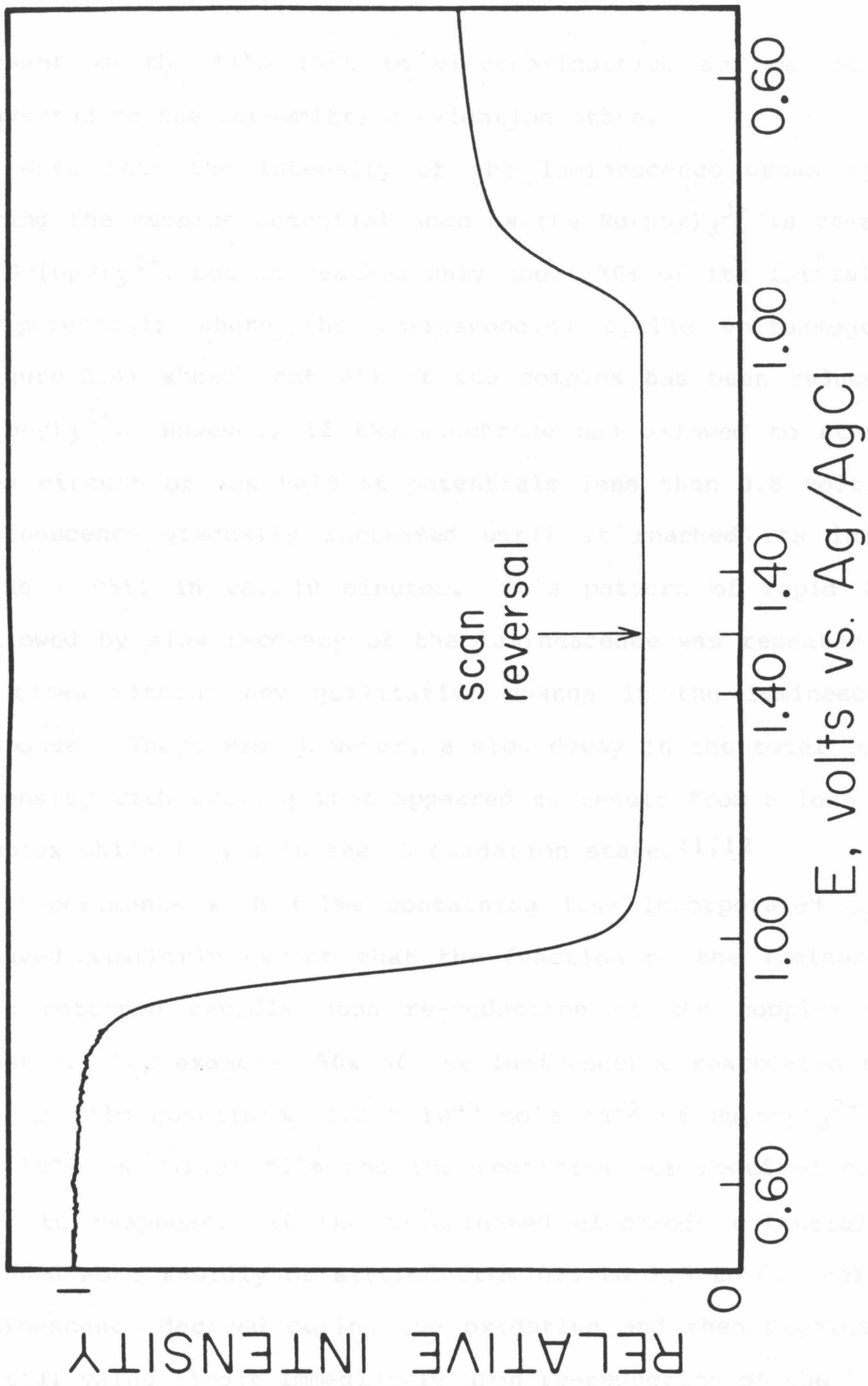
Figure 2.4 Cyclic voltammogram for 2.5 X 10^{-8} mole cm^{-2} of $Ru(bpy)_3^{2+}$ incorporated in a Nafion film (~2 X 10^{-5} cm thick) on a pyrolytic graphite electrode. Scan rate: 2 mV s^{-1}. Supporting electrolyte: 0.1 M CF_3COOH - 0.1 M CF_3COONa.


CURRENT
2μamp
0.6
0.8
1.0
1.2
1.4
E, volts vs. Ag/AgCl

because the scan rate is slow enough compared to the amount of time required for diffusion across the entire film so that the concentrations of the two halves of this redox couple are always at equilibrium with the electrode potential.[16] Thus, in the experiments which follow in which the emission from the film was monitored during the potential scan the concentrations were determined by measuring the area under the voltammogram up to each potential of interest.

Luminescence from $Ru(bpy)_3^{2+*}$ in Nafion Films. As was true of the absorption spectrum on tin oxide electrodes, the emission and excitation spectra of $Ru(bpy)_3^{2+}$ incorporated in Nafion films on graphite electrodes were essentially identical to those observed in homogeneous solution. The emission lifetime of $Ru(bpy)_3^{2+*}$ in a film on the tin oxide electrode, measured as described in the Experimental Section, was 0.68 μsec, in reasonable agreement with a value reported for the same ion in a bulk Nafion membrane under somewhat different conditions.[17] Figure 2.5 shows how the intensity of the luminescence due to $Ru(bpy)_3^{2+}$ changed when the potential of the irradiated electrode was scanned slowly (2 mV s^{-1}) from 0.5 to 1.50 volt and back. The luminescence decreases rapidly when the electrode reaches potentials where the $Ru(bpy)_3^{2+}$ is oxidized to $Ru(bpy)_3^{3+}$ which does not luminesce. The luminescence falls to a small, potential-independent value that represents the emission by the small fraction of the $Ru(bpy)_3^{2+}$

Figure 2.5 Intensity of the luminescence of the film of Figure 2.4 relative to its value at 0.5 volt vs. the potential of the graphite electrode on which the film resides.


RELATIVE INTENSITY
0
0.60
1.00
1.40
1.40
1.00
0.60
E, volts vs. Ag/AgCl
scan
reversal

present in the film that is electro-inactive and cannot be converted to the non-emitting oxidation state.

Note that the intensity of the luminescence grows again during the reverse potential scan as the $Ru(bpy)_3^{3+}$ is re-reduced to $Ru(bpy)_3^{2+}$, but it reaches only about 30% of its initial value at potentials where the corresponding cyclic voltammogram (Figure 2.4) shows that all of the complex has been reduced to $Ru(bpy)_3^{2+}$. However, if the electrode was allowed to stand at open circuit or was held at potentials less than 0.8 volt, the luminescence gradually increased until it reached its initial value (>95%) in ca. 10 minutes. This pattern of rapid loss followed by slow recovery of the luminescence was repeated 40 to 50 times without any qualitative change in the luminescent response. There was, however, a slow decay in the total emission intensity with cycling that appeared to result from a loss of the complex while it was in the +3 oxidation state.[11,12]

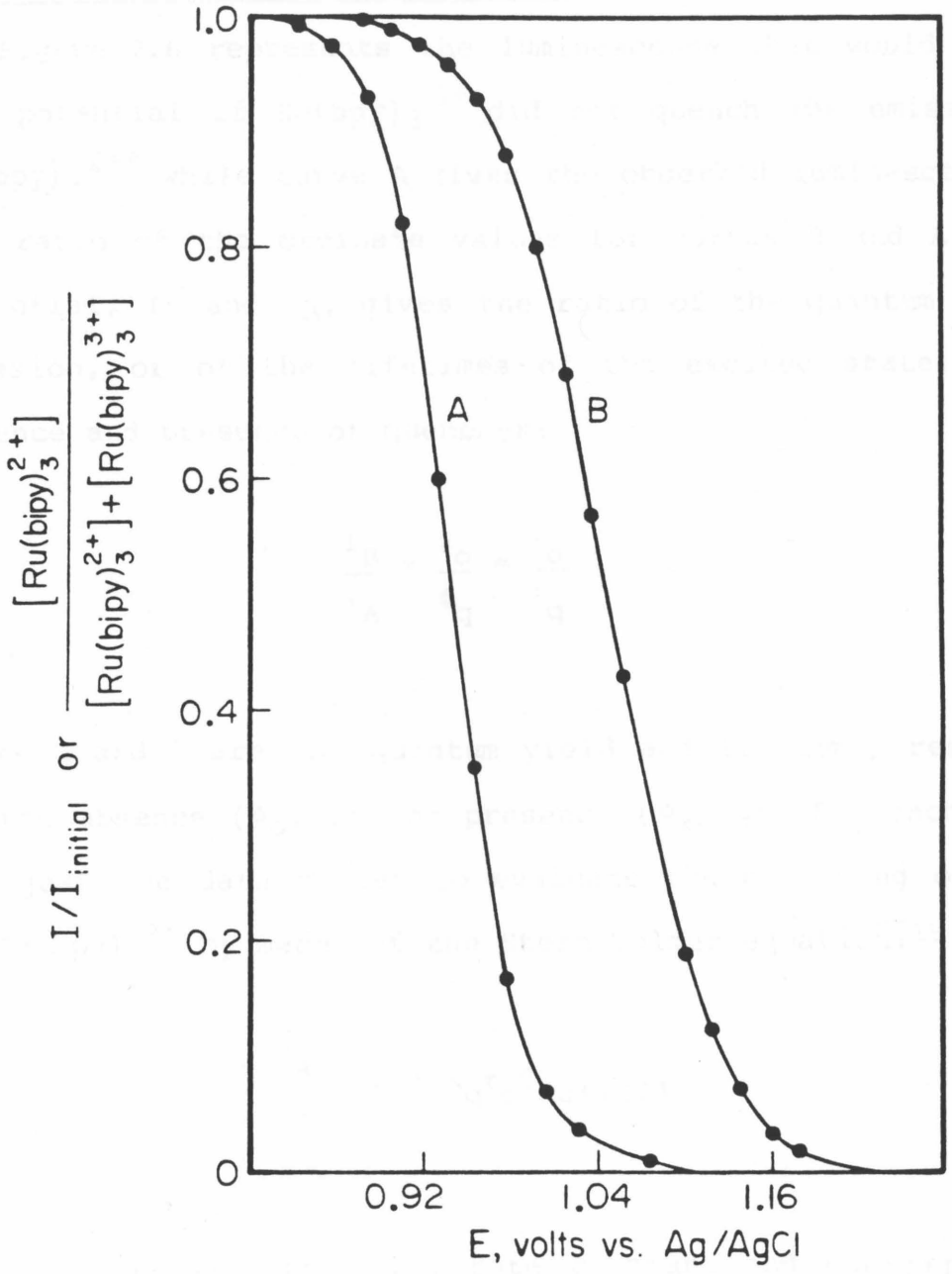
Experiments with films containing less incorporated complex behaved similarly except that the fraction of the luminescence that returned rapidly upon re-reduction of the complex was greater. For example, 50% of the luminescence reappeared rapidly with a film containing 3.2×10^{-9} mole cm^{-2} of $Ru(bpy)_3^{2+}$ in a 2×10^{-5} cm Nafion film and the remaining 50% required ca. 10 min. to reappear. If the illuminated electrode potential was scanned more rapidly or stepped from 0.5 to 1.3 to 0.5 volt, the luminescence decayed during the oxidation and then regained its initial value almost immediately upon re-reduction of the

complex. Thus, the temporary decrease in emission intensity is related to the time the complex spends as $Ru(bpy)_3^{3+}$ within the Nafion film as well as to its concentration. If only a portion of the $Ru(bpy)_3^{2+}$ was oxidized by restricting the electrode potential to values on the rising portion of the voltammogram before returning to 0.5 volt, the return of the luminescence was somewhat more rapid than when all of the incorporated complex was oxidized. The possible origin of this interesting behavior will be addressed in the Discussion Section.

As the total quantity of $Ru(bpy)_3^{2+}$ incorporated in a Nafion film was decreased, the fraction of the initial luminescence that remained when the electrode was stepped to 1.3 volt increased. Thus, the fraction of electro-inactive complex increases as its concentration in the Nafion film is decreased. Martin et al.[18] have reached a similar conclusion on the basis of electrochemical assays of Nafion films containing known amounts of $Ru(bpy)_3^{2+}$.

A plot of the concentration of $Ru(bpy)_3^{2+}$ in the film as a function of the electrode potential was prepared for comparison with the luminescence-potential curve of Figure 2.5. The two curves are plotted together in Figure 2.6 from which it is apparent that the luminescence decreases much more rapidly than does the concentration of $Ru(bpy)_3^{2+}$. It is proposed that the quenching of $Ru(bpy)_3^{2+*}$ by the $Ru(bpy)_3^{3+}$ that is introduced into the film as $Ru(bpy)_3^{2+}$ is oxidized is responsible for the separation between the two curves in Figure 2.6.

Figure 2.6 Potential dependence of: (A) the relative luminescence intensity of Figure 2.5 (corrected by subtracting the residual intensity at 1.5 volt); (B) the fraction of the total complex incorporated in the Nafion film that is present as $Ru(bpy)_3^{2+}$.


1.0
0.8
0.6
0.4
0.2
0
A
B
0.92
1.04
1.16
E, volts vs. Ag/AgCl
I/I initial or [Ru(bipy)3 2+] / ([Ru(bipy)3 2+] + [Ru(bipy)3 3+])

Electrochemical Stern-Volmer Plots. The proposal is that curve B in Figure 2.6 represents the luminescence that would result at any potential if $Ru(bpy)_3^{3+}$ did not quench the emission from $Ru(bpy)_3^{2+*}$ while curve A gives the observed luminescence. Thus, the ratio of the ordinate values for curves B and A at each potential, I_B and I_A, gives the ratio of the quantum yields for emission, or of the lifetimes of the excited state, in the absence and presence of quencher:

$$\frac{I_B}{I_A} = \frac{\Phi_o}{\Phi_q} = \frac{\tau_o}{\tau_q} \qquad (2.2)$$

where ϕ and τ are the quantum yield and lifetime, respectively, in the absence (ϕ_o, τ_o) and presence (ϕ_q, τ_q) of quencher. These are just the data needed to evaluate the quenching of $Ru(bpy)_3^{2+*}$ by $Ru(bpy)_3^{3+}$ by means of the Stern-Volmer equation:[19]

$$\frac{I_B}{I_A} = 1 + k_q \tau_o C_{Ru(III)} \qquad (2.3)$$

where k_q is the quenching rate constant and $C_{Ru(III)}$ is the concentration of the proposed quencher, $Ru(bpy)_3^{3+}$. The value of $C_{Ru(III)}$ was determined at each potential by integration of the current that flowed when the fully reduced film was scanned to that potential. (The film thickness must also be known.) Note that since the ratio of the luminescence in the presence and

absence of quencher is evaluated at each potential, eqn. (2.3) should be applicable to the experiments of Figure 2.6 even though the concentrations of both the emitter and quencher are different at each electrode potential.

Stern-Volmer plots[19] of (I_B/I_A) vs. $C_{Ru(III)}$ for two films containing different total quantities of incorporated complex are shown in Figure 2.7. The good linearity of the data supports the proposal that the luminescence of $Ru(bpy)_3^{2+*}$ is quenched by $Ru(bpy)_3^{3+}$. The values of k_q obtained from the slopes of lines in Figure 2.7A and 2.7B are 5 X 10^7 and 1 X 10^7 M^{-1} s^{-1}, respectively. This degree of reproducibility in measured values of k_q for runs with different electrodes and coatings was typical.

Quenching constants were also evaluated from excited state lifetime measurements with films in which the concentrations of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ were controlled by holding the electrode for several minutes at each potential of interest and then quickly transferring the electrode to the lifetime-measuring apparatus (Experimental Section). Figure 2.8 shows the resulting Stern-Volmer plot of (τ_o/τ_q) vs. $C_{Ru(III)}$ which was evaluated from Figure 2.3 and a knowledge of Γ_T. The slope of the line corresponds to k_q = 0.5 X 10^7 M^{-1} s^{-1}. This value is in reasonable agreement with the values obtained from Figure 2.7 and it is probably the most reliable for several reasons. i) The Nafion film was cast on a smooth tin oxide electrode so that its thickness could be measured with the profilometer. With the

Figure 2.7 Stern-Volmer plots of the ratio of the ordinate values at each potential in Figure 2.6 (see text) vs. the concentration of $Ru(bpy)_3^{3+}$ in the film. The films contained (A) 2.5×10^{-8} and (B) 3.2×10^{-9} mole cm^{-2} of complex.

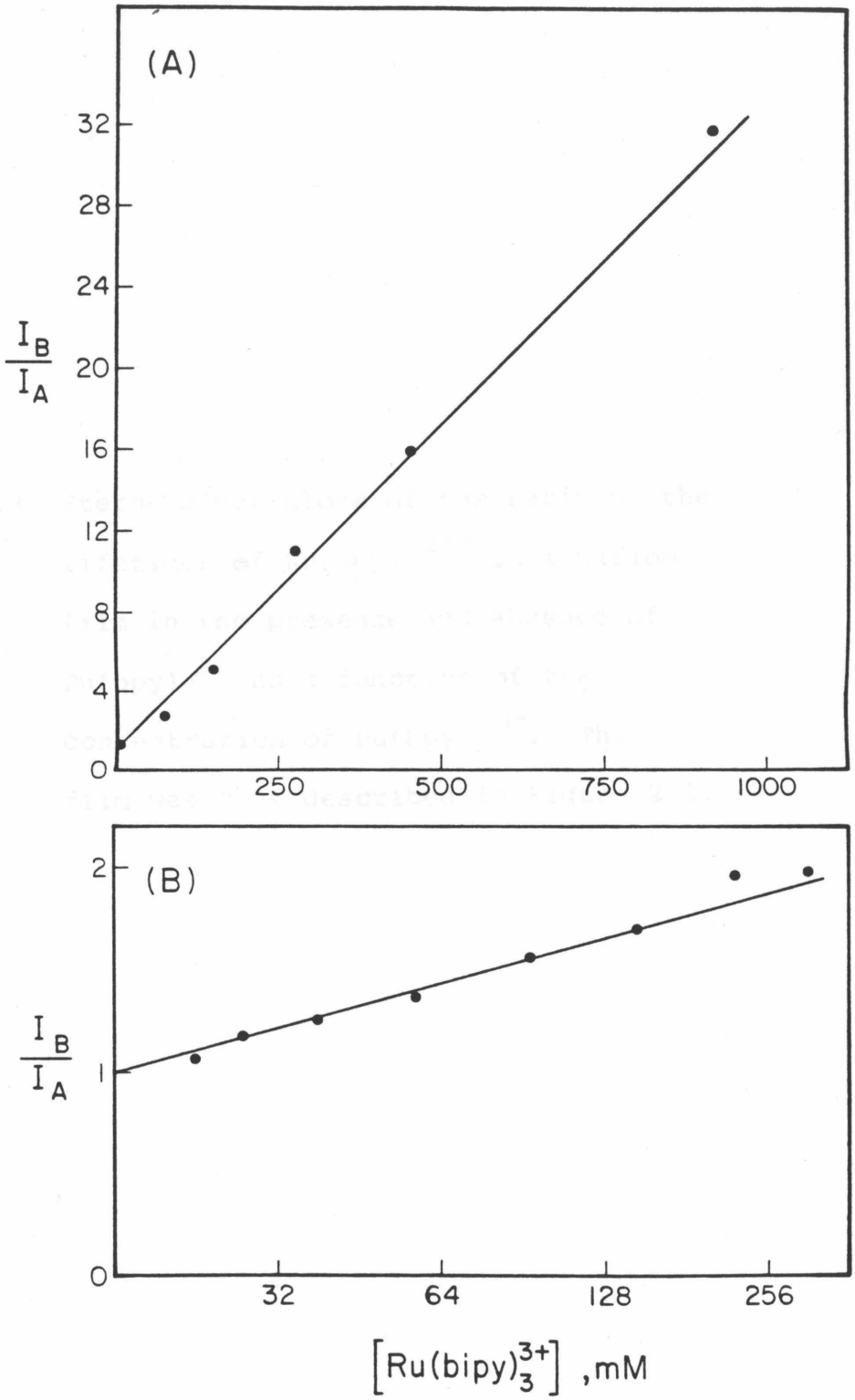
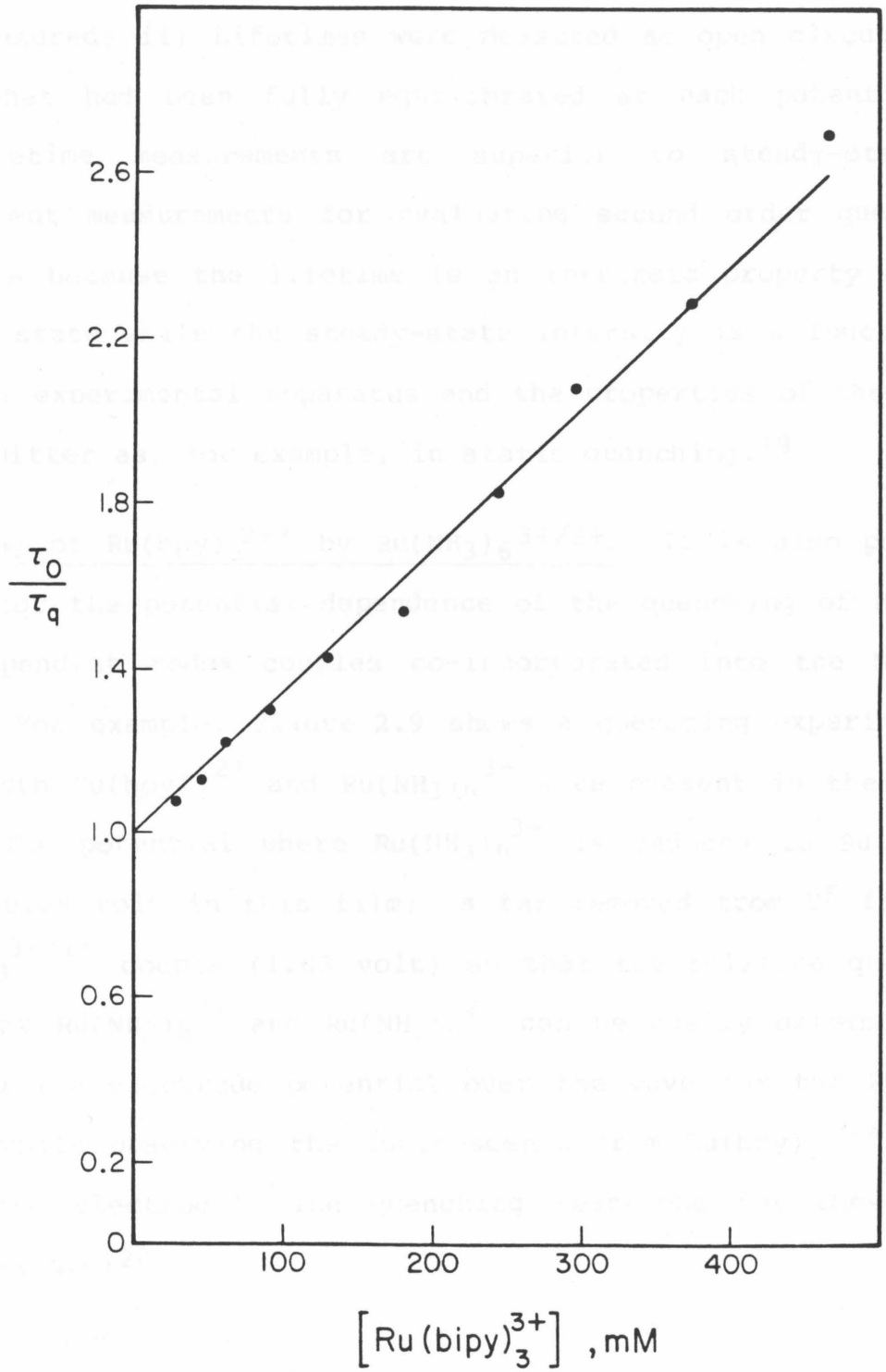

(A)
32
28
24
20
16
12
8
4
0
$\frac{I_B}{I_A}$
250
500
750
1000
(B)
2
1
0
$\frac{I_B}{I_A}$
32
64
128
256
$[Ru(bipy)_3^{3+}]$,mM

Figure 2.8 Stern-Volmer plots of the ratio of the lifetimes of $Ru(bpy)_3^{2+*}$ in a Nafion film in the presence and absence of $Ru(bpy)_3^{3+}$ as a function of the concentration of $Ru(bpy)_3^{3+}$. The film was that described in Figure 2.2.

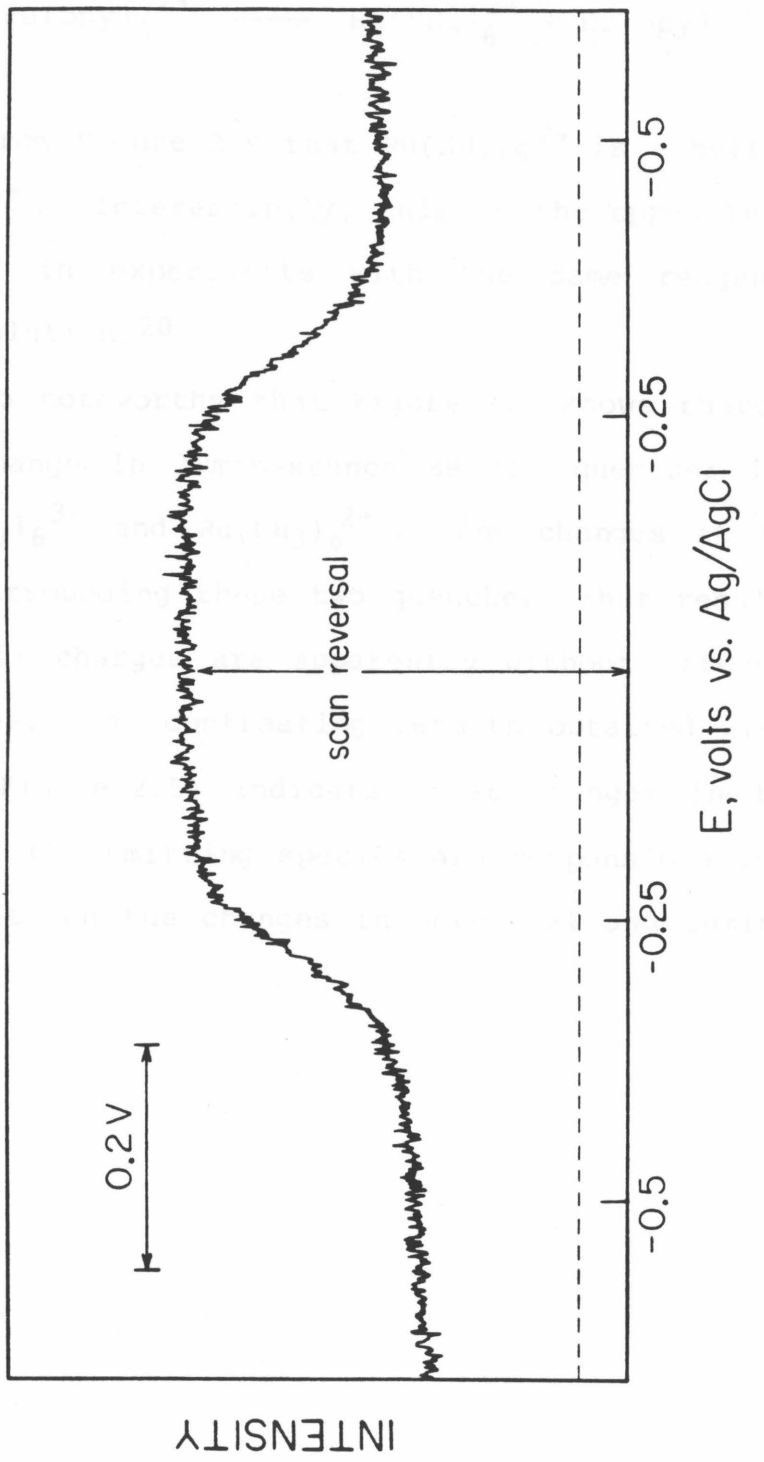

2.6
2.2
1.8
1.4
1.0
0.6
0.2
0
$\frac{\tau_0}{\tau_q}$
100
200
300
400
$[Ru(bipy)_3^{3+}]$, mM

pyrolytic graphite electrode the thickness was calculated rather than measured; ii) Lifetimes were measured at open circuit with films that had been fully equilibrated at each potential; iii) Lifetime measurements are superior to steady-state luminescent measurements for evaluating second order quenching constants because the lifetime is an intrinsic property of the excited state while the steady-state intensity is a function of both the experimental apparatus and the properties of the ground state emitter as, for example, in static quenching.[19]

Quenching of $Ru(bpy)_3^{2+*}$ by $Ru(NH_3)_6^{3+/2+}$. It is also possible to monitor the potential dependence of the quenching of $Ru(bpy)_3^{2+*}$ by independent redox couples co-incorporated into the Nafion films. For example, Figure 2.9 shows a quenching experiment in which both $Ru(bpy)_3^{2+}$ and $Ru(NH_3)_6^{3+}$ were present in the Nafion film. The potential where $Ru(NH_3)_6^{3+}$ is reduced to $Ru(NH_3)_6$ (E^f = -0.28 volt in this film) is far removed from E^f for the $Ru(bpy)_3^{3+/2+}$ couple (1.03 volt) so that the relative quenching rates for $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$ can be easily determined by scanning the electrode potential over the wave for the $Ru(NH_3)_6^{3+/2+}$ couple while observing the luminescence from $Ru(bpy)_3^{2+*}$ on the irradiated electrode. The quenching reactions for these two complexes are:[20]

$$Ru(NH_3)_6^{2+} + Ru(bpy)_3^{2+*} \longrightarrow Ru(NH_3)_6^{3+} + Ru(bpy)_3^{+} \qquad (2.4)$$

Figure 2.9 Intensity of the luminescence (arbitrary units) from a Nafion film on a graphite electrode in which ca. 5 X 10^{-9} mole cm^{-2} of both $Ru(bpy)_3^{2+}$ and $Ru(NH_3)_6^{3+}$ had been incorporated. The electrode potential was scanned between -0.65 and 0 volt at 2 mV s^{-1}. The dashed line is the residual luminescence when the electrode is held at 1.3 volt. Other conditions as in Figure 2.3.


INTENSITY
0.2 V
-0.5
-0.25
scan reversal
-0.25
-0.5
E, volts vs. Ag/AgCl

$$Ru(NH_3)_6^{3+} + Ru(bpy)_3^{2+*} \longrightarrow Ru(NH_3)_6^{2+} + Ru(bpy)_3^{3+} \qquad (2.5)$$

It is clear from Figure 2.9 that $Ru(NH_3)_6^{2+}$ is a better quencher than $Ru(NH_3)_6^{3+}$. Interestingly, this is the opposite order from that observed in experiments with the same reagents in homogeneous solution.[20]

It is also noteworthy that Figure 2.9 shows there to be no lag in the change in luminescence as the quencher is cycled between $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$. Any changes in the local environment surrounding these two quenchers that results from the change in their charges are apparently without effect on their quenching rates. The contrasting results obtained with $Ru(bpy)_3^{3+}$ as quencher (Figure 2.5) indicates that changes in the local environment of the emitting species are responsible for the much greater lag between the changes in potential and luminescence in this case.

DISCUSSION

The luminescence of $Ru(bpy)_3^{2+*}$ incorporated in Nafion films has provided a useful means of detecting apparent changes in the local environment experienced by the reactant when it is oxidized from $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$. The delay in the restoration of the full initial luminescence from $Ru(bpy)_3^{2+}$ after it has been cycled through the $Ru(bpy)_3^{3+}$ state (Figure 2.5) seems best interpreted as arising from differences between the initial local environment of $Ru(bpy)_3^{2+}$ produced by reduction of $Ru(bpy)_3^{3+}$ and the equilibrium environment that results when the $Ru(bpy)_3^{2+}$ is introduced by allowing the ion to diffuse into the Nafion film. The slow recovery of the initial luminescence cannot be attributed to some residual $Ru(bpy)_3^{3+}$ that temporarily escapes re-reduction and acts as a quencher because the faradaic charges consumed in the oxidation and re-reduction steps (as determined from the area under the cyclic voltammogram by extrapolating the current ahead of the wave to correct for the background current) are essentially equal (>95%) so that the maximum possible quantity of unreduced $Ru(bpy)_3^{3+}$ is far too small to quench the luminescence by the extent that is observed. Instead, we believe that the increase in "electrostatic cross-linking"[21] produced by the association of each $Ru(bpy)_3^{3+}$ complex with three sulfonate groups within the Nafion polyelectrolyte film results in a significant change in the local structure of the polymer. The effective local concentration of sulfonate may become larger and

this may lead to alterations in the degree of solvation of the complex. It is well known that luminescence lifetimes are dependent on the nature of the solvent.[22]

Previous studies[17,18,23] have reported evidence of at least two kinds of binding sites in Nafion membranes, one type being more hydrophilic and the other more hydrophobic. It is believed that the luminescence experiments in the present work reveal the presence of a similar kind of site anisotropy that is induced by the electrochemical increase in the charge of the cations that occupy the sites. Note that the measurements of the emission lifetime of $Ru(bpy)_3^{2+*}$ as a function of electrode potential (Figure 2.8) are not expected to have been influenced by the slow restoration of the luminescence because the experiments were conducted with fully equilibrated films.

A study of the luminescence from $Ru(bpy)_3^{2+*}$ incorporated in bulk Nafion membranes and its quenching by methylviologen cations (N,N'-dimethyl-4,4'-bipyridine) has been previously reported.[17] Non-linear Stern-Volmer plots were obtained in this case that were interpreted in terms of inhomogeneous concentrations of the incorporated cations arising from the anisotropic cluster structure of bulk Nafion membranes.[24,25] The analysis of Lee and Meisel[17] indicates that with $k_q = 10^7\ M^{-1}\ s^{-1}$ and the wide range of quencher (i.e., $Ru(bpy)_3^{3+}$) concentrations available in the electrochemical Stern-Volmer experiment (10^{-2} - 1M) inhomogeneous concentrations of the quencher caused by clustering within the Nafion films should produce significant non-linearities in

Stern-Volmer plots. Thus, the good linearity observed in Figures 2.7 and 2.8 indicates that the films cast on tin oxide or graphite surfaces from solutions of the soluble form of Nafion adopt internal structures that are more homogeneous than those present in bulk Nafion membranes. The cast films may also be considerably more porous than bulk Nafion which could account for the otherwise surprising observation of Rubinstein and Bard[6] that oxalate anions easily penetrated their Nafion films. The structures available from Nafion polyelectrolytes seem to depend strongly on the conditions employed in the preparation of membranes and the casting of films.

The extraordinary (and highly useful) stability of Nafion films on graphite and tin oxide electrodes contrasts with their behavior on glass: films cast on microscope slides are dislodged by immersion in water. This observation implies that Nafion films must rely on favorable hydrophobic interactions with the substrate if the films are to be stable. The hydrophilic nature of the surface of glass precludes such an interaction leading to poor stability. Recent experiments reveal that strongly acidic (50% H_2SO_4) solutions dislodge Nafion films from tin oxide electrodes while leaving those on graphite electrodes intact. This is exactly as predicted if strong hydrophobic interactions are needed for film stability.

The value of k_q evaluated in this work can be used to help distinguish among the various schemes considered by Rubinstein and Bard in discussing the potential dependence of the

electrochemiluminescence they observed when $Ru(bpy)_3^{2+}$ in Nafion films was oxidized to $Ru(bpy)_3^{3+}$ in the presence of oxalate anions.[6] One of the intermediates produced in the oxidation of oxalate by $Ru(bpy)_3^{3+}$ is CO_2^-,[26] a powerful reductant. This species may produce $Ru(bpy)_3^{2+*}$ directly as shown in reaction (2.6)

$$Ru(bpy)_3^{3+} + CO_2^- \longrightarrow Ru(bpy)_3^{2+*} + CO_2 \qquad (2.6)$$

or indirectly as shown in reactions (2.7) and (2.8).[26]

$$Ru(bpy)_3^{2+} + CO_2^- \longrightarrow Ru(bpy)_3^{+} + CO_2 \qquad (2.7)$$

$$Ru(bpy)_3^{3+} + Ru(bpy)_3^{+} \longrightarrow Ru(bpy)_3^{2+*} + Ru(bpy)_3^{2+} \qquad (2.8)$$

Rubinstein and Bard considered not only reactions (2.6) - (2.8) in their analysis[6] but also the quenching reaction of $Ru(bpy)_3^{3+}$ with $Ru(bpy)_3^{2+*}$ and some secondary reactions of CO_2^-. The digital simulation procedure they employed produced acceptable fits of the experimental data for three alternative sets of rate constants for several of the key reactions so that an unambiguous mechanistic assignment was not possible. The values of k_q producing the three best fits were 0, 5×10^7 and 2×10^9 M^{-1} s^{-1}. The second is closest to the values measured in these experiments and this prompts us to assign the mechanistic scheme that corresponds to this value in the digital simulation of reference (6) as the

correct one. One consequence of this assignment is that the $Ru(bpy)_3^{2+*}$ generated in the experiments of Rubenstein and Bard[6] must have arisen from the reduction of $Ru(bpy)_3^{3+}$ by both CO_2^- and $Ru(bpy)_3^+$.

CONCLUSIONS

The spectroelectrochemical procedure employed here to measure the concentrations of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ in Nafion films on transparent tin oxide electrodes is reliable and especially useful in cases where redox couples that do not adhere to the Nernst equation are under study. The use of polymer films on electrodes to house emitting and quenching species in Stern-Volmer experiments is attractive because the concentration of quencher can be varied continuously by control of the electrode potential. In favorable cases, data for an entire Stern-Volmer plot can be obtained in a single experiment. The example presented in these experiments involved the quenching of the luminescence from one-half of a redox couple by the other half of the same couple but the procedure is also applicable to cases in which the quenching is by an independent redox couple (Figure 2.9).

The results of luminescence quenching experiments proved useful in probing the structures of Nafion films as the earlier work of Lee and Meisel[17] suggested they might be. The experiments indicate that cast Nafion films have more homogeneous structures than bulk membranes of Nafion. They also show that significant changes in the local polyelectrolyte environment accompany the oxidation of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ in Nafion films. The magnitude of the quenching rate constant measured in the Nafion films allows a choice to be made among possible mechanistic schemes proposed previously[6] for the generation of electrochemiluminescence at Nafion coated electrodes.

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CHAPTER III

Effects of Electron Exchange on Charge Propagation in Nafion Films

INTRODUCTION

The mechanism by which electric charge traverses polymeric films containing uniformly distributed sites that may be oxidized and reduced has attracted considerable attention recently.[1-19] The original proposal of Kaufman and Engler[1] for polymers with anchored redox sites was that the charge is carried by electrons that hop between adjacent oxidized and reduced sites within the polymer. The same type of mechanism may apply to charge transfer through polyelectrolyte films into which ionic redox groups have been incorporated by ion exchange (electrostatic binding).[5-19] However, molecular diffusion of the electrostatically bound ions through the polymer film in which the attracting counter-ions are anchored provides an alternative charge conduction mechanism.[12]

In the general case, both mechanisms of charge propagation may operate to create a situation in redox polymer films entirely similar to that envisaged by Dahms[20] in his discussion of "electronic conduction" in aqueous solutions of redox couples. Dahms explained how electron hopping between redox ions in solution can increase the diffusion constant measured for ions that can participate in such electron self-exchange reactions. The work of Ruff and co-workers[21] and Lengyel[22] resulted in the

following equation[23] relating the measured diffusion coefficient, D_{exp}, and the diffusion coefficient, D_o, that would be measured in the absence of any electron self-exchange reaction:

$$D_{exp} = D_o + \frac{2}{3} k_{ex} \delta^2 C \qquad (3.1)$$

where k_{ex} is the second order rate constant (M^{-1} s^{-1}) governing the self-exchange reaction, C is the sum of the concentrations of the oxidized and reduced forms of the redox couple and δ is the distance between the centers of the ions when the electron exchange occurs. In ordinary homogeneous solutions contributions to ionic diffusion from electron self-exchange reactions are encountered only under unusual circumstances because D_o is typically much larger than the second term in eqn. (3.1).[21] In redox polymer films, however, much smaller values of D_o are observed[6-19] so that a significant contribution from, or even dominance by, electron hopping is possible.

According to equation (3.1), whenever electron self-exchange makes a significant contribution to the diffusion process, D_{exp} should exhibit a linear dependence on the concentration, C. However, in a very recent study of the diffusion of $Ru(bpy)_3^{2+}$ (bpy = 2,2' - bipyridine) within Nafion coatings on electrode surfaces, the value of D_{exp} was found to be essentially independent of the concentration of $Ru(bpy)_3^{2+}$.[14,15] This was surprising because there is strong evidence that charge transport

through films containing this ion is enhanced by electron self-exchange.[14,15]

In this chapter, the question of whether electron self-exchange contributes to charge transport in Nafion films is addressed by comparing the rates of charge transport through these films for two pairs of isomorphous redox couples. Each pair consists of a redox couple having a known high rate of electron self-exchange ($Ru(bpy)_3^{3+/2+}$ and $Ru(NH_3)_6^{3+/2+}$) and a structurally similar couple with a much smaller self-exchange rate ($Co(bpy)_3^{3+/2+}$ and $Co(NH_3)_6^{3+/2+}$, respectively). The diffusion coefficient of $Ru(bpy)_3^{2+}$ in the presence of $Ru(bpy)_3^{3+}$ is shown to be enhanced by electron self-exchange, although the predicted dependence on concentration is not observed, both observations being corroborated by the recent work of Bard and co-workers.[14,15] The diffusion of $Ru(NH_3)_6^{3+}$ in the presence of $Ru(NH_3)_6^{2+}$ is shown to be entirely due to molecular diffusion, with little or no contribution from electron self-exchange.

The behavior of $Co(bpy)_3^{2+}$ is examined in greater detail and, in particular, its diffusion coefficient is measured electrochemically both by oxidizing it to $Co(bpy)_3^{3+}$ and by reducing it to $Co(bpy)_3^{+}$. Much larger values of D_{exp} obtain when the $Co(bpy)_3^{2+/+}$ couple is involved than when the electroactive couple is $Co(bpy)_3^{3+/2+}$, even though the same species, $Co(bpy)_3^{2+}$, is "diffusing" in both cases. In addition, the larger values of D_{exp} which are observed with the $Co(bpy)_3^{2+/+}$ couple exhibit a clear concentration dependence of the type

predicted by equation (3.1). An interpretation of this behavior is proposed which also leads to a rationalization for the absence of a concentration dependence in D_{exp} for $Ru(bpy)_3^{2+}$.

EXPERIMENTAL

Materials. A 5.2 wt.% solution of Nafion in a 5/1 mixture of isopropanol/water (available from a sample supplied by E. I. du Pont de Nemours Company a number of years ago) was used to prepare electrode coatings. $Co(bpy)_3Cl_2$ was synthesized and purified essentially as described by Burstall and Nyholm.[24] $Co(NH_3)_6Cl_3$ was synthesized and purified according to standard procedures.[25] $Ru(bpy)_3Cl_2$ (G. F. Smith Chemical Co.) and $Ru(NH_3)_6Cl_3$ (Matthey Bishop, Inc.) were recrystallized from water before use. Other chemicals were reagent grade and were used as received. Deionized water from a Barnstead Nanopure purification train was used to prepare all solutions. Basal plane pyrolytic graphite electrodes (Union Carbide Co., Chicago, Ill.) were cut and mounted as previously described.[5] A standard two-compartment electrochemical cell was employed. The calomel reference electrode was saturated with sodium chloride. All potentials are quoted with respect to this reference electrode (SSCE).

Procedures and Instrumentation. Nafion films were prepared on the graphite electrodes as described in Chapter II. In the studies comparing the charge transport rates within the two pairs of redox couples, the dried and washed films were exposed to pure solutions of the multiply-charged cationic complexes to incorporate them by ion exchange. In the more detailed studies of the concentration dependence of D_{exp} for $Co(bpy)_3^{2+}$ the

incorporation of this complex was accomplished by exposing the coated electrodes to a 1.0 mM aqueous solution of the complex for times ranging from 10 seconds to 10 minutes. In order to allow measurements of D_{exp} at various reactant concentrations in the same film, measurements were commenced at low reactant concentrations and repeated after the concentration was increased by exposing the electrode to the reactant solution for an additional time. After each successive loading of the film it was allowed to soak for 30 minutes in pure supporting electrolyte solution to allow the reactant concentration profile to become more uniform. The quantities of complex incorporated were determined by potential step coulometry as previously described.[8] Diffusion coefficients of the incorporated complexes within the polymer film were determined by chronocoulometry[6] after transferring the electrodes to solutions of pure supporting electrolytes.

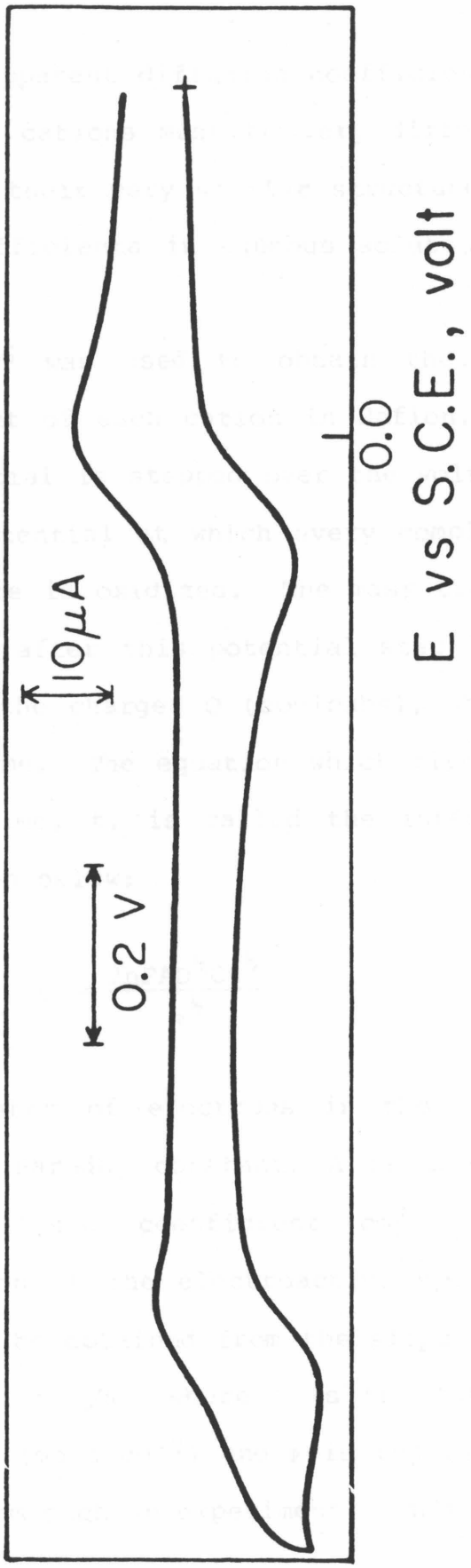
For cyclic voltammetry and coulometry a Princeton Applied Research Model 173/179 potentiostat/digital coulometer was employed along with a Model 175 universal programmer. Chronocoulometric data were obtained using a computer controlled apparatus previously described.[26]

The film thicknesses resulting from evaporation of both 2 μl and 4 μl aliquots of the 5.2% Nafion solution were measured with a Sloan Detak profilometer. The thickness of a 4 μl film was measured both before and after loading the film with $Co(bpy)_3^{2+}$ up to concentrations of ca. 1 M. The film thickness did not depend on the concentration of the incorporated complex.

RESULTS

Comparative Studies. Figure 3.1 shows the cyclic voltammogram that resulted after a Nafion coated pyrolytic graphite electrode was soaked for 10 minutes in a solution containing 1.0 mM $Co(bpy)_3^{2+}$ and 0.1 mM $Ru(bpy)_3^{2+}$, washed and transferred to a pure supporting electrolyte solution (0.2 M CF_3COONa at pH 3.3). The reversible responses of the $Co(bpy)_3^{3+/2+}$ and $Ru(bpy)_3^{3+/2+}$ couples incorporated by the Nafion film are evident at 0.10 and 1.03 volt, respectively. Both waves are stable to hours of repetitive cycling showing that the anionic Nafion film holds the incorporated cations very strongly. Similar behavior has been previously reported in the case of $Ru(bpy)_3^{2+}$ in Nafion films by Bard and co-workers.[13-15] The asymmetric shapes of the voltammetric waves indicate that the responses are controlled by diffusional motions within the film.[27,28] These motions could be the physical transport of the incorporated cations themselves but coupled motions of counter ions and of the polymer chain segments are also possibilities.[28] A coulometric assay[8] of the film showed that 2.5×10^{-8} mole cm^{-2} of $Co(bpy)_3^{2+}$ and 1.9×10^{-9} mole cm^{-2} of $Ru(bpy)_3^{2+}$ had been incorporated. These two structurally similar cations thus enter the film in approximately the same ratio as their bulk concentrations in the loading solution. However, the peak currents of the two waves in Figure 3.1 differ by less than a factor of 2 despite the almost thirteen-fold difference in the concentrations of the two reactants. It

Figure 3.1 Cyclic voltammetry $Co(bpy)_3^{3+/2+}$ and $Ru(bpy)_3^{3+/2+}$ incorporated in a Nafion coating on a pyrolytic graphite electrode. The Nafion coating was cast from 5 $\mu\ell$ of the coating solution and contained 1.5×10^{-6} mole cm^{-2} of sulfonate groups, 2.5×10^{-8} mole cm^{-2} of $Co(bpy)_3^{2+}$ and 1.9×10^{-9} mole cm^{-2} of $Ru(bpy)_3^{2+}$. Supporting electrolyte: 0.2 M CF_3COONa at pH 3.3. Scan rate: 100 mV s^{-1}. Cathodic currents are upward; positive potentials to the left.


10μA
0.2 V
0.0
E vs S.C.E., volt

is clear that the apparent diffusion coefficients governing the behavior of the two cations must be very different within the Nafion film despite their very similar structures and essentially equal diffusion coefficients in aqueous solution (6×10^{-6} cm^2 s^{-1}).[13]

Chronocoulometry[6] was used to obtain the value of the diffusion coefficient of each cation in Nafion. In this method the electrode potential is stepped over the voltammetric wave for the complex to a potential at which every complex which reaches the electrode surface is oxidized. The mass transport controlled current which flows after this potential step is electronically integrated to give the charge, Q (coulombs), which is monitored as a function of time. The equation which gives the value of Q as a function of time, t, is called the integrated Cottrell equation and is given below:

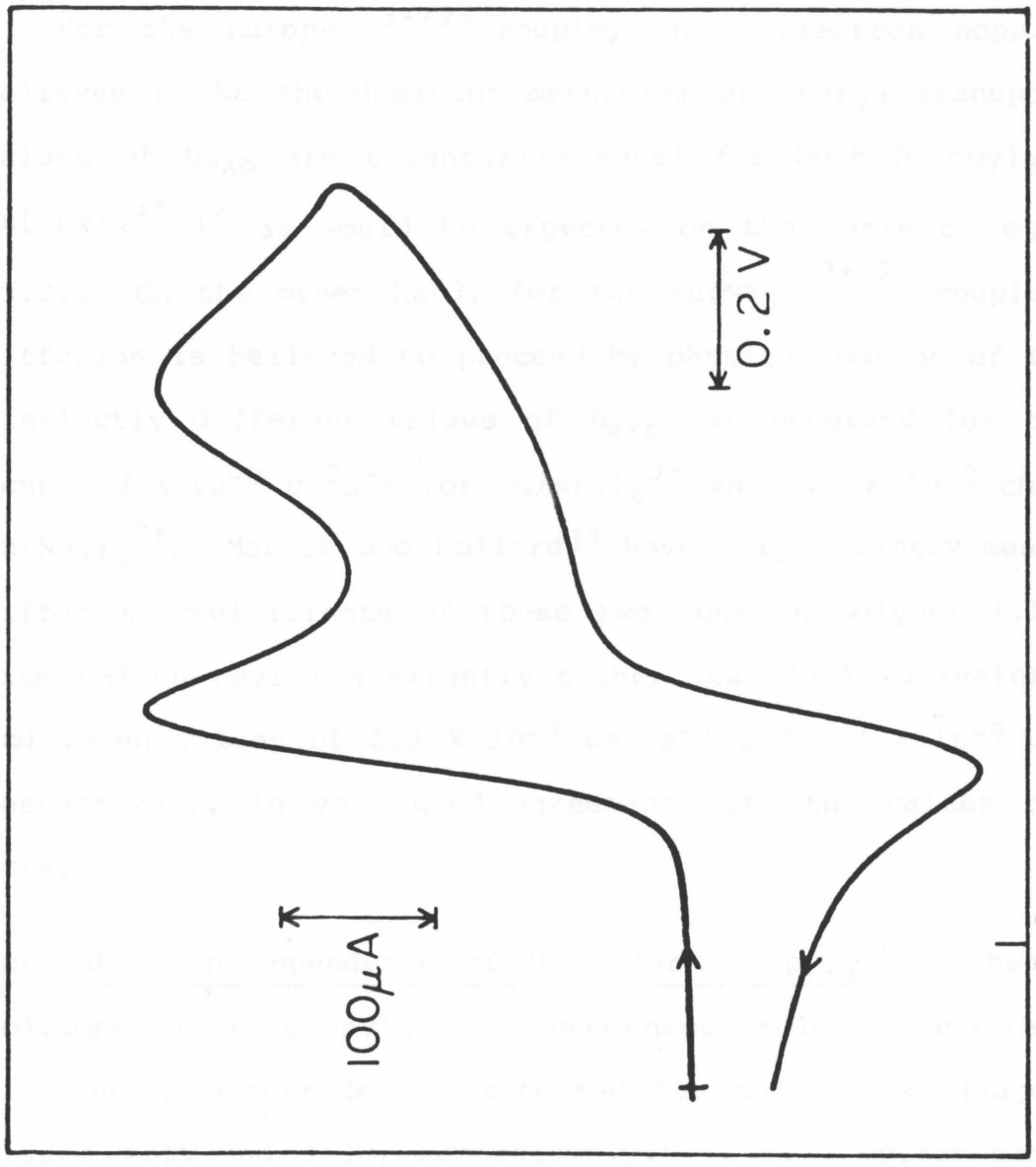
$$Q = \frac{2nFAD^{\frac{1}{2}}Ct^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \qquad (3.2)$$

where n is the number of electrons in the electrochemical reaction, F is the Faraday constant, A is the electrode area (cm^2), D is the diffusion coefficient (cm^2 s^{-1}) and C is the initial concentration of the electroactive species (mole cm^{-3}). The product $D^{\frac{1}{2}}C$ may be obtained from the slope of a plot of Q vs. $t^{\frac{1}{2}}$. Knowing that $C = \Gamma/\Phi$, where Γ is the total quantity of complex in the film (mole cm^{-2}) and Φ is the film thickness (cm), one may obtain D from such an experiment. This technique was

used to obtain the diffusion coefficient of each cation in the Nafion film using Nafion coatings in which only a single cation was incorporated. The values obtained were 2 X 10^{-12} cm^2 s^{-1} for $Co(bpy)_3^{2+}$ and 4 X 10^{-10} cm^2 s^{-1} for $Ru(bpy)_3^{2+}$. This remarkably large difference in the diffusion coefficients of two such similar ions argues strongly that their diffusion within the Nafion films proceeds by differing mechanisms. It is proposed that the key difference lies in the relative rates of electron self-exchange exhibited by the two complexes: The electron self-exchange rate constant for $Co(bpy)_3^{3+/2+}$ is 2 $M^{-1}s^{-1}$;[29] that for $Ru(bpy)_3^{3+/2+}$ is 2 X 10^9 $M^{-1}s^{-1}$.[30]

A similar comparison was also carried out for $Ru(NH_3)_6^{3+}$ and $Co(NH_3)_6^{3+}$ incorporated in Nafion films. Figure 3.2 shows the cyclic voltammogram for a film into which both complexes were introduced. The reversible response of the $Ru(NH_3)_6^{3+/2+}$ couple contrasts with the irreversible response of $Co(NH_3)_6^{3+/2+}$ which rapidly decomposes upon reduction to yield unoxidizable products. There is no possibility for an enhancement of D_{exp} by electron self-exchange between $Co(NH_3)_6^{3+}$ and $Co(NH_3)_6^{2+}$ before the latter decomposes because k_{ex} is $<10^{-10}$ $M^{-1}s^{-1}$.[31] For $Ru(NH_3)_6^{3+/2+}$, on the other hand, k_{ex} is 4 X 10^3 $M^{-1}s^{-1}$.[32] For this couple, electron self-exchange could result in a significant contribution to D_{exp} if D_o were small enough in the Nafion film. However, the experimentally measured diffusion coefficient for both $Co(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{3+}$ was ca. 2 X 10^{-9} cm^2s^{-1}. The equality of these two values of D_{exp} despite the negligible contribution from

Figure 3.2 Cyclic voltammetry of $Ru(NH_3)_6^{3+}$ and $Co(NH_3)_6^{3+}$ incorporated in a Nafion coating on a pyrolytic graphite electrode. The cations were incorporated by soaking the coated electrode for 10 minutes in a solution containing 1 mM $Ru(NH_3)_6Cl_3$ and $Co(NH_3)_6Cl_3$. Other conditions as in Figure 3.1, except the pH of the supporting electrolyte was 6.

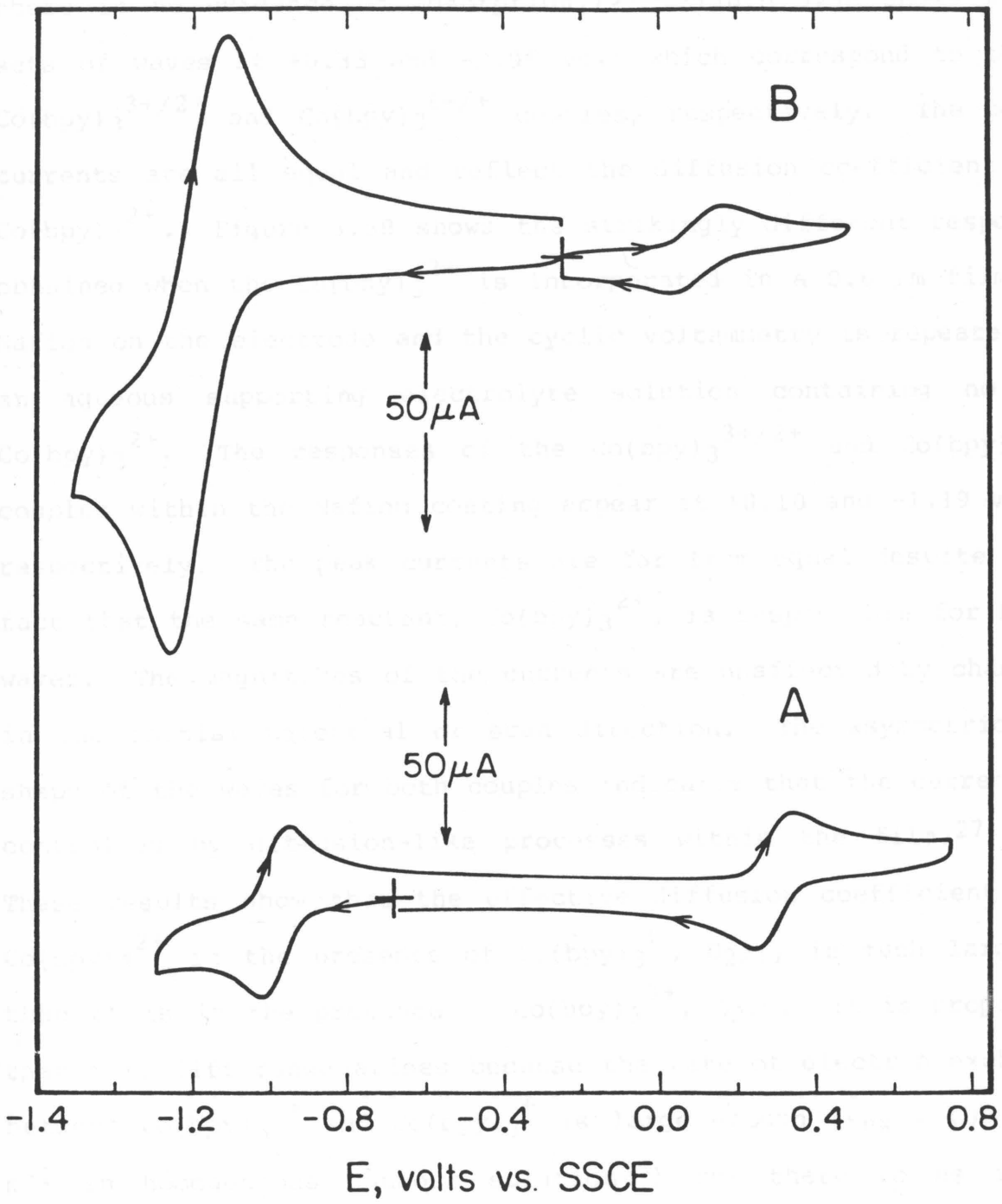

0.2 V
100μA
0.0
E vs S.C.E.

electron hopping in the case of $Co(NH_3)_6^{3+}$ seems clearly to demonstrate that electron self-exchange makes no contribution to the diffusion of either ion in the film: 2×10^{-9} cm^2s^{-1} represents the common value of D_o for both cations.

For the $Ru(bpy)_3^{3+/2+}$ couple, where electron hopping is believed to be the dominant mechanism of charge transport, the values of D_{exp} are essentially equal for both $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ [15] as would be expected on the basis of equation (3.2). On the other hand, for the $Ru(NH_3)_6^{3+/2+}$ couple, where diffusion is believed to proceed by physical motion of the ions, distinctly different values of D_{exp} are observed for the two ions: 2×10^{-9} cm^2s^{-1} for $Ru(NH_3)_6^{3+}$ and 3.6×10^{-9} cm^2s^{-1} for $Ru(NH_3)_6^{2+}$. Martin and Dollard[33] have very recently measured the diffusion coefficients of these two ions in polymer films cast from Nafion having a slightly higher (ca. 13%) equivalent weight and found values of 2.3×10^{-9} cm^2 s^{-1} and 3.4×10^{-9} cm^2 s^{-1}, respectively, in very good agreement with the values reported here.

Concentration Dependence of D_{exp} for $Co(bpy)_3^{2+}$. The cyclic voltammetry of $Co(bpy)_3^{2+}$ in homogeneous solution and in a Nafion film on an electrode is presented for comparative purposes in Figure 3.3A and 3.3B, respectively. (Cyclic voltammograms for $Co(bpy)_3^{2+}$ recorded at uncoated electrodes in aqueous solution are distorted by the adsorption of the 2+ complex and the low solubility of the 1+ complex. For this reason its behavior at an

Figure 3.3 Cyclic voltammograms for $Co(bpy)_3^{2+}$.
(A) 0.5 mM $Co(bpy)_3^{2+}$ in acetonitrile recorded at a bare graphite electrode. Supporting electrolyte: 0.1 M tetraethylammonium perchlorate.
(B) $Co(bpy)_3^{2+}$ incorporated in a Nafion coating (0.6 μm) on a graphite electrode. The concentration of complex in the coating is ca. 1 M. The two voltammograms were recorded in separate experiments in pure supporting electrolyte: 0.5 M Na_2SO_4. Scan rate: 100 mV s^{-1} throughout.


B
50μA
A
50μA
-1.4
-1.2
-0.8
-0.4
0.0
0.4
0.8
E, volts vs. SSCE

uncoated graphite electrode was examined in acetonitrile where there is no evidence of adsorption.)[34] Figure 3.3A shows two sets of waves at +0.33 and -0.96 volt which correspond to the $Co(bpy)_3^{3+/2+}$ and $Co(bpy)_3^{2+/+}$ couples, respectively. The peak currents are all equal and reflect the diffusion coefficient of $Co(bpy)_3^{2+}$. Figure 3.3B shows the strikingly different response obtained when the $Co(bpy)_3^{2+}$ is incorporated in a 0.6 μm film of Nafion on the electrode and the cyclic voltammetry is repeated in an aqueous supporting electrolyte solution containing no $Co(bpy)_3^{2+}$. The responses of the $Co(bpy)_3^{3+/2+}$ and $Co(bpy)_3^{2+/+}$ couples within the Nafion coating appear at +0.10 and -1.19 volt, respectively. The peak currents are far from equal despite the fact that the same reactant, $Co(bpy)_3^{2+}$, is responsible for both waves. The magnitudes of the currents are unaffected by changes in the initial potential or scan direction. The asymmetrical shape of the waves for both couples indicates that the current is controlled by diffusion-like processes within the film.[27,28] These results show that the effective diffusion coefficient of $Co(bpy)_3^{2+}$ in the presence of $Co(bpy)_3^{+}$, $D_{2/1}$, is much larger than it is in the presence of $Co(bpy)_3^{3+}$, $D_{2/3}$. It is proposed that this difference arises because the rate of electron exchange between $Co(bpy)_3^{2+}$ and $Co(bpy)_3^{+}$ is large enough ($k_{ex} \geq 10^8$ M^{-1} s^{-1} in homogeneous aqueous solution[35]) for there to be a significant contribution from electron hopping to the propagation of charge through the film during the reduction of $Co(bpy)_3^{2+}$.

The fact that electron exchange does not contribute to the diffusion of $Co(bpy)_3^{2+}$ in the presence of $Co(bpy)_3^{3+}$ in Nafion coatings, as demonstrated in the previous section, is in accord with the much smaller peak currents exhibited by this couple in Figure 3.3B. This is a very useful result because it allows D_o for $Co(bpy)_3^{2+}$ in Nafion coatings to be measured as a function of concentration (by oxidizing it to $Co(bpy)_3^{3+}$). Then, the contribution of electron exchange to the diffusion of the same complex can be deduced by reducing it to $Co(bpy)_3^{+}$ and subtracting the contribution arising from D_o. Thus, an internal standard for D_o is available that is immune to changes in reactant concentrations or film thicknesses. This feature is exploited extensively in the experiments to be described.

Equation (3.2) was used to evaluate D_{exp} from chronocoulometric data. Typically, measurements encompassed times from 10^{-3} to 10^{-1} s for a variety of concentrations of $Co(bpy)_3^{2+}$ and for two values of the film thickness. The concentration dependence of the slopes of the plots of charge vs $(time)^{1/2}$ was measured with the identical film for the entire set of measurements to minimize uncertainties arising from small variations in the film thickness from coating to coating.

The use of equation (3.2) relies on the assumption that the $Co(bpy)_3^{2+}$ is distributed uniformly throughout the film. To verify this assumption, a separate set of experiments was performed in which the linearity of chronocoulometric plots for the oxidation of $Co(bpy)_3^{2+}$ was examined over a time range wide

enough for the diffusion layer thickness, $(Dt)^{1/2}$, to vary from a few percent to over fifty percent of the film thickness. The plots remained linear throughout this range of diffusion layers as expected for a reactant distributed uniformly throughout the film.

Figure 3.4 shows the values of $D_{2/1}$ and $D_{2/3}$ obtained as a function of C, the concentration of $Co(bpy)_3^{2+}$, for a 0.6 μm film into which the complex was incrementally incorporated. $D_{2/1}$ undergoes a nearly five-fold increase over the concentration range examined while $D_{2/3}$ decreases by a smaller factor. The values of $D_{2/1}$ and $D_{2/3}$ tend toward a common value as C approaches zero. The increase of $D_{2/1}$ with concentration and the near equality of $D_{2/1}$ and $D_{2/3}$ at low concentrations are features that are in qualitative agreement with equation (3.1) if $D_{2/3}$ is taken as equal to D_o. The dependence of $D_{2/3}$ (i.e., D_o) on C is not predicted by equation (3.1) and this aspect of the behavior will be examined further in the Discussion section. To correct for the dependence of D_o on C in comparing the experimental data with equation (3.1) the data of Figure 3.4 were replotted in the form $D_{2/1} - D_{2/3}$ vs. C. in Figure 3.5. A similar plot for a film thickness of 1.2 μm had the same slope and intercept within the experimental reproducibility of ca. ±30%. The fact that the plots are linear and go through the origin supports the contention that the data adhere to equation (3.1) and therefore provide a means of evaluating k_{ex} for electron exchange between $Co(bpy)_3^{2+}$

Figure 3.4 Concentration dependence of diffusion coefficients for $Co(bpy)_3^{2+}$ in a 0.6 μm Nafion coating.

(●) $D_{2/1}$, measured by reducing $Co(bpy)_3^{2+}$ to $Co(bpy)_3^{1+}$;

(O) $D_{2/3}$, measured by oxidizing $Co(bpy)_3^{2+}$ to $Co(bpy)_3^{3+}$.

Supporting electrolyte: 0.5 $\underline{M}$ Na_2SO_4.

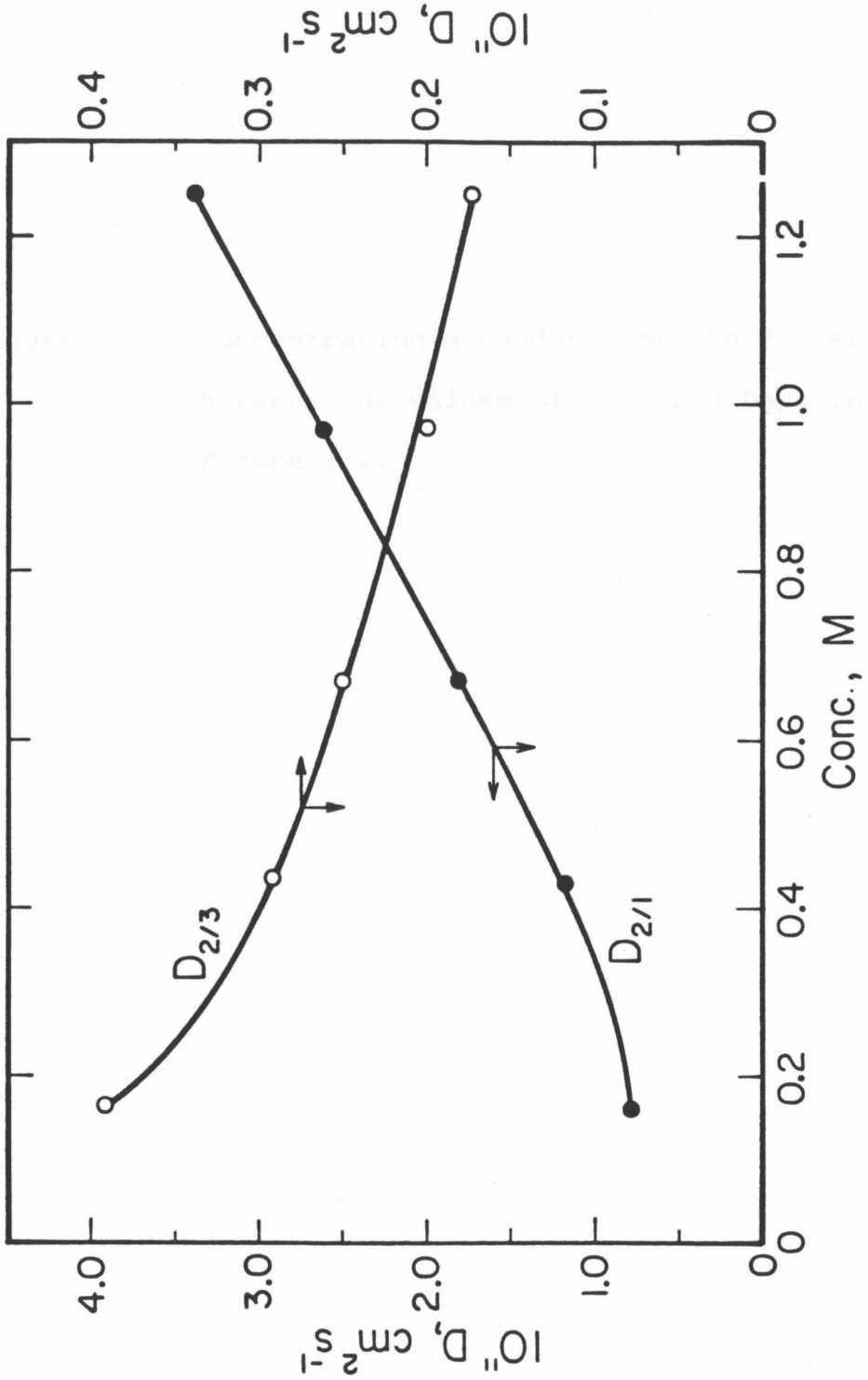
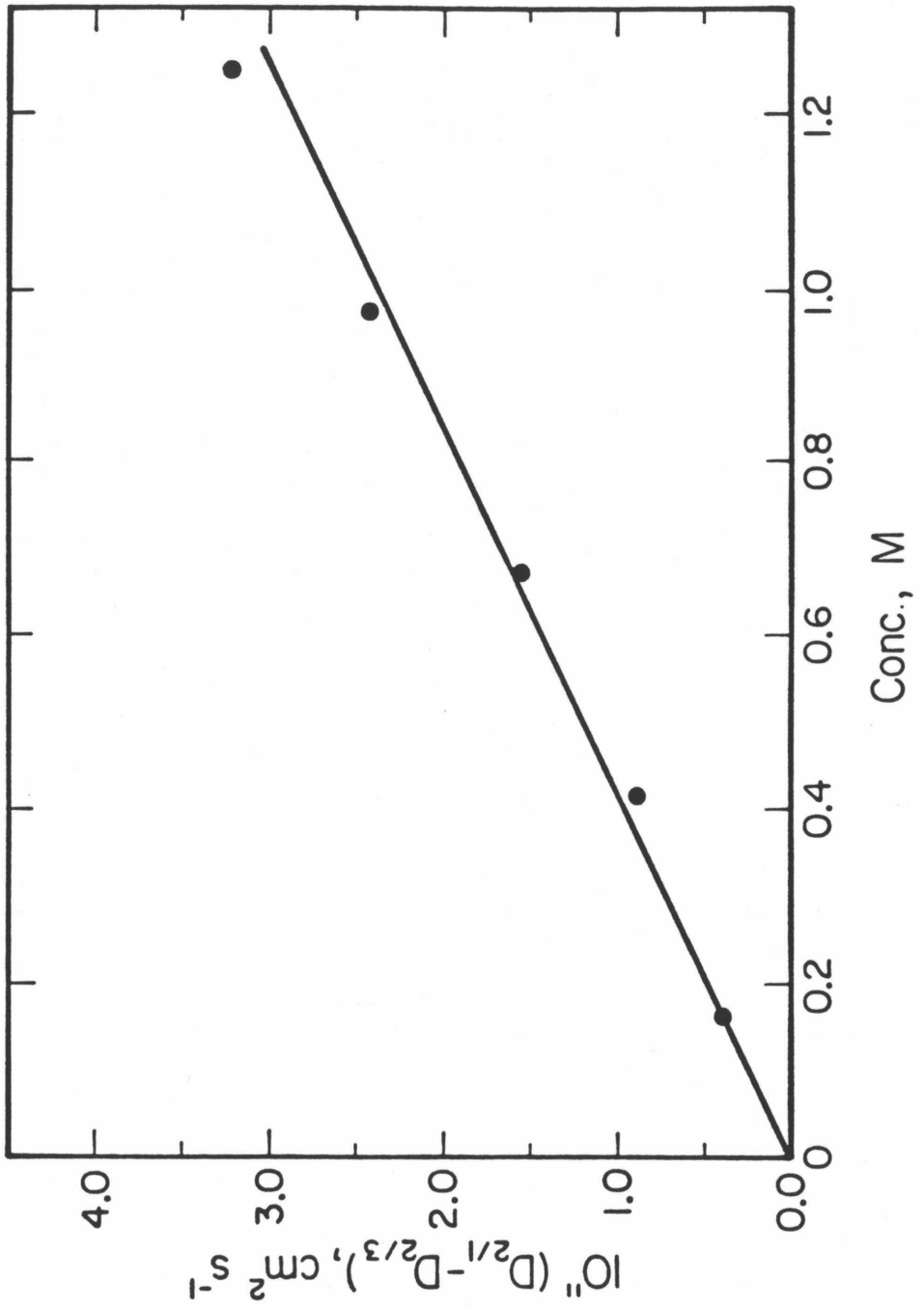

10^5 D, $cm^2 s^{-1}$
4.0
3.0
2.0
1.0
0
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1.0
1.2
Conc., M
$D_{2/3}$
$D_{2/1}$

Figure 3.5 Concentration dependence of the difference between the values of $D_{2/1}$ and $D_{2/3}$ in Figure 3.4.


10^{11} ($D_{2/1}$-$D_{2/3}$), cm^2 s^{-1}
0.0
1.0
2.0
3.0
4.0
0
0.2
0.4
0.6
0.8
1.0
1.2
Conc., M

and $Co(bpy)_3^+$ inside the Nafion coating. This analysis is presented in the Discussion section.

DISCUSSION

The results shown in Figure 3.1, along with the very different values of the diffusion coefficients measured for $Co(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$ when these complexes are oxidized in Nafion films, clearly demonstrate that electron hopping makes a major contribution to the charge transport process when $Ru(bpy)_3^{2+}$ is oxidized to $Ru(bpy)_3^{3+}$. The equality of the diffusion coefficients of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ in these measurements and those of Martin, Rubinstein and Bard[15] also alludes to this fact. That these diffusion coefficients are not dependent on the concentrations of the complexes in the Nafion films is not predicted by equation (3.1). This feature of the data will be discussed later in this Chapter.

The cyclic voltammogram in Figure 3.2 indicates that electron hopping is relatively unimportant in Nafion films containing $Ru(NH_3)_6^{3+}$ despite the fact that the electron self-exchange rate constant for the $Ru(NH_3)_6^{3+/2+}$ couple is large enough for this process to warrant consideration. The diffusion coefficients for $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$ are the two largest known values for electroactive complexes in Nafion films on electrodes,[13-15,33] and it is probably these large values of D_O which so overshadow the electron hopping rate that it is rendered negligible.

The difference in the diffusion coefficients for $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$ and the equality of the diffusion coefficients for $Ru(bpy)_3^{3+}$ and $Ru(bpy)_3^{2+}$ suggest a simple criterion for

distinguishing between electron hopping and molecular diffusion mechanisms of charge transport in polymer coatings on electrodes: Equal diffusion coefficients for the oxidized and reduced halves of the redox couple point to electron hopping. Different diffusion coefficients for the two ions may signal the dominance of molecular diffusion.

Concentration Dependence of D_{exp}. The results shown in Figures 3.4 and 3.5 seem clearly to demonstrate that the diffusion coefficient for $Co(bpy)_3^{2+}$ measured in the presence of $Co(bpy)_3^{+}$ in Nafion coatings exhibits a concentration dependence of the type that Dahms[20] and Ruff and co-workers[21] predicted to be present whenever electron self-exchange is an important component of the diffusive process. The fact that the contributions from physical motion of the $Co(bpy)_3^{2+}$ cation can be easily determined from the diffusion coefficient, $D_{2/3}$, obtained in experiments where the complex is oxidized to $Co(bpy)_3^{3+}$, makes this system unusually attractive for quantitative studies. Thus, according to equation (3.1), the slope of the line in Figure 3.5 should be equal to $2k_{ex}\delta^2/3$ from which k_{ex} can be estimated if δ is taken to be the diameter of the $Co(bpy)_3^{2+}$ complex, ca. 14 Å. The value of k_{ex} obtained in this way, 2×10^3 M^{-1} s^{-1}, is much smaller than the value of k_{ex} obtained by Brunschwig et al.[35] from measurements in homogeneous solution, $k_{ex} \geq 10^8$ M^{-1} s^{-1}. This is not surprising when it is recognized that the rate constants measured experimentally, $(k_{ex})_{obs}$, obey equation (3.3)

$$\frac{1}{(k_{ex})_{obs}} = \frac{1}{k_d} + \frac{1}{k_{ex}} \qquad (3.3)$$

where k_d is the diffusion-controlled rate constant and k_{ex} is the true self-exchange rate constant. In homogeneous solution k_d is 10^{10}-10^{11} $M^{-1}s^{-1}$ so that the measured rate constant, $(k_{ex})_{obs} \geq 10^8$ $M^{-1}s^{-1}$,[35] provides a good estimate of k_{ex}. However, the value of k_d that applies to Nafion coatings is much smaller. Its magnitude may be estimated from the measured value of $D_{2/3}$ using the form of the Smoluchowski equation[36a] appropriate for the self-exchange case:[36b]

$$k_d = \frac{2\pi N_A R D}{10^3} \qquad (3.4)$$

where N_A is Avagadro's number, and R and D are the sum of the radii and of the diffusion coefficients, respectively, of the reactants. Taking R to be 14 X 10^{-8} cm (twice the radius of $Co(bpy)_3^{2+}$) and D to be 4 X 10^{-12} cm^2s^{-1} (twice $D_{2/3}$) gives k_d = 2 X 10^3 $M^{-1}s^{-1}$. This value is much smaller than the measured value of k_{ex} in homogeneous solution so that it is clear from equation (3.3) that $(k_{ex})_{obs}$ evaluated from equation (3.1) and the slope of the line in Figure 3.5 will be determined by k_d rather than k_{ex}. The fact that the value of k_d calculated from equation (3.4), 2 X 10^3 $M^{-1}s^{-1}$, is close to the rate constant obtained from the slope of the line in Figure 3.5, 2 X 10^3 $M^{-1}s^{-1}$, strongly supports this interpretation. The

approximations involved in this calculation make quantitative conclusions unwarranted but it does seem clear that the rates of reactions which are sufficiently rapid in solution will be leveled to the diffusion-controlled rate when they are measured in polymer films which significantly impede the motion of the reactants.

Variation in $D_{2/3}$ with the Concentration of Incorporated Reactant.

The decrease in $D_{2/3}$ for $Co(bpy)_3^{2+}$ shown in Figure 3.4 occurs in concentration ranges where the thickness of the films has been shown to remain fixed. Recalling that $D_{2/3}$ measures the diffusion rate of $Co(bpy)_3^{2+}$ by physical motion of the complex and/or counter ions through the coating, it is proposed that the decrease results from competition between the diffusing complexes for counter-ionic or hydrophobic residence sites within the polyelectrolyte film. The basic phenomenon, termed "single file diffusion", was first discussed by Hodgkin and Keynes in relation to cationic transport across membranes.[37] Subsequently, numerous theoretical and experimental investigations of the phenomenon have been carried out.[38] The essential idea is that diffusing species which must move between more or less fixed sites within a matrix may have their rate of motion limited by the decreasing availability of sites as the concentration of the diffusing species increases. The experimental result is a diffusion coefficient that decreases with the concentration of the diffusing species. A lucid discussion of the model and its

consequences is given in reference 39. It seems likely that this model may prove generally useful in accounting for the motion of incorporated reactants through polymer and polyelectrolyte coatings.

Comparison with Previous Results. The diffusion coefficients that have been measured for various cations in Nafion coatings span a surprisingly large range of values. Thus, $D_{2/3}$ for $Co(bpy)_3^{2+}$ is ca. 2 X 10^{-12} cm^2s^{-1} while $D_{2/3}$ for $Ru(bpy)_3^{2+}$ is ca. 5 X 10^{-10} cm^2s^{-1},[13-15] $D_{2/3}$ for $Ru(NH_3)_6^{3+}$ is ca. 2 X 10^{-9} cm^2s^{-1} [33] and the diffusion coeffocient of Na^+ is 9 X 10^{-7} cm^2s^{-1}.[40] Among these ions, only the diffusion of $Ru(bpy)_3^{2+}$ is believed to be enhanced by electron exchange reactions[13-15] yet its diffusion coefficient does not exhibit the concentration dependence predicted in equation (3.1). What is responsible for this lack of concentration dependence and why should the diffusion of Na^+ be so much faster than that of $Ru(bpy)_3^{2+}$ despite the lack of electron exchange enhancement of the diffusion of Na^+? It is believed that the answers to these questions are to be found in the unusual structural features of Nafion that include two phases between which incorporated cations may partition. Nafion membranes are known[41] to contain regions composed mainly of fluorocarbon that are separated from largely aqueous, hydrophilic regions by a so-called interfacial region that is more hydrophobic and tends to accumulate hydrophobic cations. For example, Cs^+ ions incorporated by Nafion membranes

reside primarily in this interfacial region while Na^+ ions remain in the more hydrophilic, aqueous phase.[40] The diffusion coefficient of Cs^+ in Nafion (5×10^{-8} cm^2s^{-1}) is much smaller than that for Na^+ (9×10^{-7} cm^2s^{-1})[40] suggesting that ions confined to the hydrophobic phase diffuse more slowly than those in the hydrophilic phase.

Both $Ru(bpy)_3^{2+}$ and $Co(bpy)_3^{2+}$ are much more hydrophobic than Na^+ and would therefore be expected to partition preferentially into the more hydrophobic interfacial regions within Nafion. Indeed, $Ru(bpy)_3^{2+}$ has been shown to do so.[42] This would account for the smaller diffusion coefficient of the bipyridine complexes. However, both $D_{2/3}$ for $Ru(bpy)_3^{2+}$ and $D_{2/1}$ for $Co(bpy)_3^{2+}$ are enhanced by electron exchange but only the latter shows the concentration dependence predicted by equation (3.1). In addition, the absolute values of the two diffusion coefficients ($D_{2/3}$ for $Ru(bpy)_3^{2+}$ = 5×10^{-10} cm^2s^{-1}; $D_{2/1}$ for $Co(bpy)_3^{2+}$ = 1-5 $\times 10^{-11}$ cm^2s^{-1}) are unexpectedly disparate considering that the two dipositive ions have very similar sizes and self-exchange rate constants that are large and similar.[35] It is felt that this apparent anomaly can also be explained on the basis of the two phase structure within Nafion.

Cations that partition between the hydrophobic and hydrophilic phases within Nafion coatings diffuse within each phase with a diffusion coefficient characteristic of that phase. Exchange of cations between the two phases is slow compared to the times involved in the measurement of diffusion coefficients

(vide infra) so that the measured values represent the sum of the contributions of diffusion in each of the phases weighted by the concentration of the cation in each phase. Hydrophilic ions such as Na^+ that remain primarily in the more aqueous phase inside the Nafion coating exhibit relatively large diffusion coefficients that reflect their motion through the hydrophilic phase. Hydrophobic cations such as $Co(bpy)_3^{2+}$ partition primarily in the less aqueous phase inside the coating where much smaller diffusion coefficients prevail, e.g., 2-4 X 10^{-12} cm^2s^{-1}. Diffusion in both phases may be enhanced by electron exchange between redox couples with sufficiently large self-exchange rate constants when they are present at sufficiently high concentrations. Such in-phase electron exchange between diffusing redox couples is revealed by the concentration dependence of the observed diffusion coefficients of which the $Co(bpy)_3^{2+/+}$ couple is the first reported example.

Now consider the behavior of $Ru(bpy)_3^{2+}$. This cation will also partition between the two phases within Nafion coatings to yield a composite diffusion coefficient representing the sum of the contributions from diffusion in each phase. However, with the $Ru(bpy)_3^{3+/2+}$ couple, unlike the $Co(bpy)_3^{3+/2+}$ couple, electron exchange between the oxidized and reduced forms of the complex proceeds rapidly, and when the two forms undergoing exchange are present in different phases the exchange couples the diffusional processes occurring in each phase.[43] As a result, contributions to the measured diffusion coefficient from the

cations present in the more aqueous phase will be larger than is true for couples such as $Co(bpy)_3^{3+/2+}$ where such cross-phase (as well as in-phase) electron exchange proceeds too slowly to be important. Saveant has shown[44] that two parallel diffusional pathways that are coupled by electron exchange between the diffusing reactants will produce an apparent diffusion coefficient, D_{app}, given by equation (3.5)

$$D_{app} = D_1 f_1 + D_2 f_2 \qquad (3.5)$$

where D_1 and D_2 are the diffusion coefficients appropriate for each phase and f_1 and f_2 are the fractions of the total incorporated reactant present in each phase. The equilibrium constant, K, governing the partitioning of the ions between the two phases in which the diffusion occurs is given by $K = f_2/f_1$. The measured diffusion coefficient for $Ru(bpy)_3^{2+}$ is $D_{app} = 5 \times 10^{-10}$ cm^2s^{-1}. The diffusion coefficient of the (presumably small) fraction of the $Ru(bpy)_3^{2+}$ present in the hydrophilic phase (i.e., D_1 in equation (3.5)) cannot be measured independently but it may be approximated roughly by the reported value for Na^+, namely 9×10^{-7} cm^2s^{-1}. A reasonable estimate for the diffusion coefficient of $Ru(bpy)_3^{2+}$ within the hydrophobic phase (i.e., D_2 in equation (3.5)) is $D_{2/1}$ for $Co(bpy)_3^{2+}$, say 2×10^{-11} cm^2s^{-1}. Substitution of these values in equation (3.5) leads to a calculated value of $f_1 = 5.3 \times 10^{-4}$. Thus, this line of reasoning leads to the conclusion that even though less than

0.1% of the $Ru(bpy)_3^{2+}$ is present in the hydrophilic phase, it is this phase which carries most of the diffusional current because of the efficient coupling mechanism provided by cross-phase electron exchange.

Note that this interpretation also provides an immediate explanation for the lack of concentration dependence in the measured values of $D_{app} = D_{2/3}$ for $Ru(bpy)_3^{2+}$: If the diffusion of this ion is dominated by its relatively rapid motion in the hydrophilic phase in the Nafion where it is present at a concentration too low for in-phase electron exchange to contribute significantly to D_1, no concentration dependence of D_{app} is expected. Electron exchange doubtless <u>does</u> enhance the rate of diffusion of the majority of the $Ru(bpy)_3^{2+}$ that is partitioned into the hydrophobic phase but the resulting diffusion coefficient in this phase remains too small for this diffusional pathway to become quantitatively significant.

The much smaller value of k_{ex} for the $Co(bpy)_3^{3+/2+}$ couple means that the diffusional pathways in the hydrophobic and hydrophilic phases that contribute to the measured values of $D_{2/3}$ for this ion are not likely to be coupled by cross-phase electron exchange. In the absence of cross-phase exchange (or when it proceeds negligibly on the experimental time scale) the observed diffusion coefficient will obey equation (3.6)[44]

$$D_{app}^{\frac{1}{2}} = D_1^{\frac{1}{2}} f_1 + D_2^{\frac{1}{2}} f_2 \qquad (3.6)$$

If we assume for $Co(bpy)_3^{2+}$, as we did for $Ru(bpy)_3^{2+}$ that D_1 = 9 X 10^{-7} cm^2s^{-1} and that f_1 is the same for both $Co(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$ (f_1 = 5.3 X 10^{-4}) the $D_1^{1/2}$ f_1 term in equation (3.6) amounts to 0.05 X 10^{-6} cm $s^{-1/2}$ while $D_{app}^{1/2}$= $D_{2/3}^{1/2}$ for $Co(bpy)_3^{2+}$= 1.4 X 10^{-6} cm $s^{-1/2}$. Thus, the contribution to D_{app} from the small portion of the cations that reside in the hydrophilic phase is negligibly small so that the measured value of $D_{2/3}$ for $Co(bpy)_3^{2+}$ should provide a reasonable measure of the diffusion coefficient of the ion within the hydrophobic phase, i.e., D_2.

Note that the small measured value of $D_{2/3}$ for $Co(bpy)_3^{2+}$ could not be explained if equation (3.5) instead of equation (3.6) were used. Sufficiently rapid cross-phase place exchange reactions in which ions in opposite phases trade places with each other can also couple the two diffusional pathways.[43] The fact that the D_{app} for $Co(bpy)_3^{2+}$ is consistent with equation (3.6) but not equation (3.5) indicates that the rate of such a place exchange reaction is not great enough to affect the measured values of the diffusion coefficients.

This analysis indicates that the previous conclusion that the diffusional rate of $Ru(bpy)_3^{2+}$ is enhanced by electron exchange requires some refinement: The measured value of $D_{2/3}$ for $Ru(bpy)_3^{2+}$ in Nafion is dominated by the physical motion of the ion through the hydrophilic phase within Nafion coatings. $D_{2/3}$ for $Ru(bpy)_3^{2+}$ is larger than for $Co(bpy)_3^{2+}$ because cross-phase electron exchange between the concentrated but slower moving ions

in the hydrophobic phase and the dilute but rapidly moving ions in the hydrophilic phase allows the latter to carry most of the diffusional motion.

A final question to be faced is why $D_{2/1}$ for $Co(bpy)_3^{2+}$, where a high electron exchange rate prevails in solution, does not achieve a concentration independence by the same mechanism proposed in the case of $D_{2/3}$ for $Ru(bpy)_3^{2+}$. The answer seems likely to depend upon the greater hydrophobicity of the less highly charged $Co(bpy)_3^{+}$ ion. In aqueous solutions at bare graphite electrodes $Co(bpy)_3^{+}$ readily leaves the aqueous phase to form multiple adsorbed (or precipitated) layers on the surface.[45] Precipitation of the $Co(bpy)_3^{+}$ generated in the hydrophilic phase in Nafion could both slow down the rate of cross-phase electron exchange and decrease the effective concentration in the hydrophilic phase of the reactant ions whose higher mobility needs to be exploited to achieve a concentration independent diffusion coefficient.

CONCLUSIONS

One of the primary conclusions resulting from this study is that the previously demonstrated[40,41] two-phase structure of Nafion should not be ignored in constructing mechanistic schemes to account for charge propagation through Nafion coatings. Combination of the present data with those from previous related studies[13-15,33] and ideas arising from investigations of diffusion in membranes[37-39] suggests that at least two classes of diffusional behavior, as measured electrochemically, are likely to be encountered with redox reactants that diffuse through Nafion coatings. The first class is comprised of reactants with electron self-exchange rates too small to affect the diffusion process significantly. Their diffusion involves physical motion of the reactant at rates that differ greatly in the hydrophilic and hydrophobic phases within the Nafion coatings. Competition between reactant species for residence sites within the coating may produce diffusion coefficients that decrease with the reactant concentration as anticipated by the model of single file diffusion.[39] The $Co(bpy)_3^{3+/2+}$ couple and the $Co(NH_3)_6^{3+/2+}$ and $Ru(NH_3)_6^{3+/2+}$ couples are examples of reactants of this class.

The second class of possible systems involves reactants for which electron self-exchange proceeds rapidly enough to affect the diffusional rates. Because of the two-phase structure adopted by Nafion coatings the electron exchange may involve both

in-phase and cross-phase exhanges. In-phase exchange involves reactants that are both present in the same phase while cross-phase electron exchange involves reactants that are in different phases inside the coating. (Cross-phase place exchange is also possible[43,44] but is apparently rather slow in Nafion coatings as judged by the behavior of the $Co(bpy)_3^{3+/2+}$ couple.) In-phase electron exchange enhances diffusional rates in the way described by Dahms[20] and Ruff et al.[21] and produces diffusion coefficients that increase with the reactant concentration. Cross-phase electron exchange couples the diffusional processes in each phase. The concentration dependence of the measured diffusion coefficients, if any, will depend on the equilibrium concentrations and relative diffusion coefficients of the reactants in each phase. $D_{2/3}$ for $Ru(bpy)_3^{2+}$ is believed to be a case in which cross-phase electron exchange enhances the measured diffusion coefficient while $D_{2/1}$ for $Co(bpy)_3^{2+}$ is the first case in which in-phase electron exchange makes its presence evident in the form of a concentration-dependent diffusion coefficient.

The diffusion of reactants within polymeric coatings on electrodes is usually considerably slower than in homogeneous solution. As a result, rate constants evaluated within polymeric coatings for inherently rapid electron exchange reactions are often leveled to the diffusion-controlled rate constant characteristic of the diffusion of the reactant in the polymer. In such cases the values of rate constants for electron transfer reactions measured in homogeneous solution will exceed the values

measured in polymer coatings even when the ions are equally reactive towards electron transfer in both media. This factor may be expected to affect the observed rates of both self-exchange and cross-reactions occurring in the interior of polymeric coatings.

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CHAPTER IV

Enhancement of Charge Transport Rates by Electron Exchange Cross-reactions within Nafion Films

INTRODUCTION

Chapter III presented a model of charge transport in Nafion in which the rapidly diffusing complexes in the hydrophilic phase carry charge to the more slowly moving complexes in the hydrophobic phase. The electron self-exchange reaction between the fast and slow species couples their diffusion leading to larger currents than would be observed in the absence of such coupling. An interesting and potentially fruitful (see Chapter V) extension of this idea is the possible enhancement of charge transport rates by electron exchange cross-reactions between two different couples incorporated in the same polymer film. The key requirement for there to be a significant enhancement in the current as a result of the cross-reaction is that one of the redox couples (the mediator) have a much larger diffusion coefficient in the polymer film than the other couple. This type of enhancement is only rarely observed in homogeneous solutions at bare electrodes because the range of diffusion coefficients for different compounds in solution is much smaller (10^{-5} - 10^{-6} cm^2 s^{-1}) than the range observed for diffusion through polymer films (10^{-6} - 10^{-12} cm^2 s^{-1} in Nafion).

Miller and co-workers[1] were the first to clearly formulate and demonstrate this type of charge transport mediation using a hydroquinone-based, electroactive polymer as the slow species and bis(hydroxymethyl)ferrocenium as the fast species. For thick films of this polymer they found that only a small percentage of the anchored hydroquinone moieties (approximately one monolayer) could be oxidized at positive electrode potentials, probably because of a sluggish electron exchange reaction between the anchored redox sites.[1] They showed that by incorporating a ferrocene derivative in the film and scanning the electrode potential to values sufficient to oxidize it, the mobile ferrocene derivative could mediate the oxidation of up to 200 monolayers of the hydroquinone polymer. Facci and Murray[2] examined $IrCl_6^{3-}/Fe(CN)_6^{3-}$ mixtures electrostatically incorporated into a polycationic film on an electrode and presented qualitative evidence for mediation of charge transport to each redox couple by the other. In this case the diffusion coefficients of the two complexes in the film were quite similar[2] so the observed enhancement of the current by the coupling was quite small. In a different study, White et al.[3] incorporated osmium tris(2,2'-bipyridine) dication, $Os(bpy)_3^{2+}$, and $Ru(bpy)_3^{2+}$ together into a Nafion film and observed no apparent enhancement of the charge transport rate to $Os(bpy)_3^{2+}$ by $Ru(bpy)_3^{3+}$ even though the diffusion coefficient they reported for the ruthenium complex is almost 6 times larger than that for the osmium complex.[3] These studies and the results in Chapter III indicated

both that charge transport mediation in polymer films is observable and that more quantitative studies are in order.

This chapter describes studies in which Nafion films containing (a) $Ru(NH_3)_6^{3+}$, (b) cobalt(III) bis(2,2',2" - terpyridine), $Co(tpy)_2^{3+}$, and $Ru(NH_3)_6^{3+}$ and (c) $Co(tpy)_2^{2+}$ and ferrocenylmethyl(trimethylammonium) cation, $FcTMA^+$ are examined using cyclic voltammetry and chronocoulometry. The cyclic voltammetric results clearly show that the diffusion of the pairs of complexes in (b) and (c) above are coupled by electron exchange cross-reactions. The chronocoulometric results from the $Ru(NH_3)_6^{3+}/Co(tpy)_2^{3+}$ system are used to quantitatively compare the coupled currents to those observed for each ion in the absence of the other.

EXPERIMENTAL

Materials and Instrumentation. A 5.2 wt. % solution of Nafion (supplied by E. I. du Pont de Nemours Co. a number of years ago) diluted ten-fold with isopropanol was used to prepare the electrode coatings. The $Co(tpy)_2 Cl_2$ was generously donated by Dr. Brian Willett. FcTMA ClO_4 was prepared by metathesis of FcTMA Br (Research Organic/Inorganic Chemical Corp.) with $NaClO_4$ followed by recrystallization from water. $Ru(NH_3)_6Cl_3$ (Matthey Bishop, Inc.) was used as received. $Co(tpy)_2^{3+}$ solutions were prepared by electrolysis of $Co(tpy)_2^{2+}$ in 0.5 M Na_2SO_4. The supporting electrolyte in all experiments was 0.5 M Na_2SO_4. All solutions were made using water from a Barnstead Nanopure purification train. Basal plane pyrolytic graphite (BPG) electrodes were cut and mounted as previously described.[4] A standard two-compartment electrochemical cell was employed. The calomel reference electrode was saturated with NaCl. All potentials are reported with respect to this reference electrode (SSCE). The instrumentation used was as described in Chapter III.

Procedures. Nafion films were prepared by evaporation of 8 µl of the 0.52% coating solution on the surface of a BPG electrode with a surface area of 0.174 cm^2. Solutions of the complexes with concentrations between 4 X 10^{-7} M and 4 X 10^{-5} M were prepared by using a Hamilton 10 µl syringe to transfer aliquots of millimolar solutions of the complexes into 0.5 M Na_2SO_4. After some initial

cyclic voltammetric scans to "break in" the films, the Nafion coated BPG electrodes were allowed to come to equilibrium with these dilute solutions before any measurements were made. This required approximately 20 minutes for the $Ru(NH_3)_6^{3+}$ solutions, 1½ hours for the $FcTMA^+$ solutions and 6-7 hours for the $Co(tpy)_2^{3+}$ and $Co(tpy)_2^{2+}$ solutions. After this equilibration the films were very stable while kept in the dilute complex solutions, with repeated oxidation and reduction of the incorporated complexes having no apparent effect on the cyclic voltammetric response. It should be emphasized here that all measurements were made in these dilute complex solutions. This avoids the problem of leaching of the complexes from the films if the electrodes were transferred to pure supporting electrolyte solutions to make the measurements. The cyclic voltammetric and chronocoulometric experiments are certainly immune to possible problems resulting from this practice because the complexes in solution are present at such low concentrations. However, the coulometric measurements may somewhat overestimate the film loadings. It is felt that the alternative procedure of transferring to pure supporting electrolyte solutions for the coulometric measurements would give even grosser underestimations of the film loadings, especially in cases in which the complexes in the films rapidly equilibrate with the solution, as with $Ru(NH_3)_6^{3+}$.

For films containing only $Ru(NH_3)_6^{3+}$ the quantity of incorporated complex, Γ (mole cm^{-2}), was measured by manually integrating a slow (5mV s^{-1}) cyclic voltammogram under thin-layer

conditions[5] as in Chapter II. In these experiments the difference between the integrals of the forward and reverse waves was never greater than 10% indicating that the $Ru(NH_3)_6^{2+}$ is stably held within the film on the time scale of the experiment. In order to obtain the values of Γ for $FcTMA^+$, Γ_{Fe}, and for $Co(tpy)_2^{3+}$ or $Co(tpy)_2^{2+}$, Γ_{Co}, when both were present in the film the following procedure was employed. The potential was stepped over both waves (from -0.2 V to 0.5 V) and the current which passed was integrated until it fell to background levels (45-60 min.). This charge was taken as a measure of $\Gamma_{Fe} + \Gamma_{Co}$. Next the potential was stepped to a value at which the $FcTMA^{2+}$ was reduced to $FcTMA^+$ but the $Co(tpy)_2^{3+}$ remained oxidized (0.2 V). After the film was fully equilibrated with the solution and the current had fallen to background levels the potential was stepped back to 0.5 V to oxidize all of the $FcTMA^+$ to $FcTMA^{2+}$. In this way the charge required for exhaustive oxidation of the $FcTMA^+$ could be measured without interference from $Co(tpy)_2^{2+}$ oxidation. This charge was taken as a measure of Γ_{Fe}, Γ_{Co} being obtained by simple subtraction. The assumption is made here that the amount of $FcTMA^+$ incorporated into the film is independent of the oxidation state of the cobalt complex. This is probably not a good assumption, but, unfortunately it is not possible to obtain Γ_{Fe} in the presence of $Co(tpy)_2^{2+}$.

A similar procedure was followed for obtaining $\Gamma_{Ru} + \Gamma_{Co}$ for the $Ru(NH_3)_6^{3+}/Co(tpy)_2^{3+}$ films. However, because the formal potentials of the $Ru(NH_3)_6^{3+/2+}$ and $Co(tpy)_2^{3+/2+}$ couples in the

Nafion film are 50mV closer together than those of $FcTMA^{2+/+}$ and $Co(tpy)_2^{3+/2+}$ it was not possible to choose a potential at which the cobalt complex was entirely reduced and the ruthenium complex entirely oxidized. Thus, in order to determine Γ_{Ru} the following procedure was employed. After exhaustive reduction of both complexes at -0.4 V the electrode potential was stepped back to -0.15 V. At this potential all of the ruthenium complex was oxidized but some of the cobalt complex was also present in the oxidized form. A slow cyclic voltammogram from -0.15 V to -0.4 V gave a large irregularly shaped wave resulting from the reduction of both the $Ru(NH_3)_6^{3+}$ and the fraction of the cobalt present as $Co(tpy)_2^{3+}$. However, on the return scan a symmetric peak was observed for the oxidation of $Ru(NH_3)_6^{2+}$, unperturbed by the presence of $Co(tpy)_2^{2+}$. This wave was manually integrated and taken as a measure of Γ_{Ru}, using the same assumption as for the iron complex, that the extent of incorporation was independent of the cobalt oxidation state.

All measurements were made on solutions which had been deaerated by bubbling with O_2-scrubbed argon for at least 45 minutes. This special precaution was taken to exclude dioxygen from the cell because of the long integration times and negative potentials required for the coulometric experiments.

RESULTS

The experimental strategy employed in this study was two-fold. First, cyclic voltammetric studies were used to show qualitatively that the mediators, $Ru(NH_3)_6^{2+}$ and $FcTMA^{2+}$, could carry charge to the slower moving species, $Co(tpy)_2^{3+}$ and $Co(tpy)_2^{2+}$, respectively. Then a quantitative study of the $Ru(NH_3)_6^{3+}/Co(tpy)_2^{3+}$ system was undertaken. Chronocoulometric data were obtained (as in Chapter III) on the charge transport rate of each complex in the Nafion film. These data were then combined with the measured values of Γ_{Ru} and Γ_{Co} to calculate what the chronocoulometric slope would have been in the absence of coupling in an experiment in which both $Ru(NH_3)_6^{3+}$ and $Co(tpy)_2^{3+}$ were simultaneously reduced. Finally, these calculated values were compared with those obtained from experiment. The enhancement of the experimental chronocoulometric slopes over the calculated ones gives a measure of how effectively the electron exchange cross-reaction between $Ru(NH_3)_6^{2+}$ and $Co(tpy)_2^{3+}$ couples their diffusion.

By employing a method in which chronocoulometric slopes are compared, this study does not require that the thickness of the polymer film be known. The only values needed for the analysis are the chronocoulometric slopes and the values of Γ for the various species. The next section reports these values for a Nafion film containing increasing amounts of $Ru(NH_3)_6^{3+}$.

Determination of Incorporation Isotherm and Chronocoulometric Slope for $Ru(NH_3)_6^{3+}$. Figure 4.1 shows a typical cyclic voltammogram for a Nafion film after equilibration with a 12 X 10^{-6} M solution of $Ru(NH_3)_6^{3+}$. The symmetric shape of the waves and the very small (ca. 20 mV) peak separation attest to the fact that thin-layer conditions prevail at this scan rate.[5] Thus, Γ_{Ru} may be obtained by integration of one of the cyclic voltammetric waves. This procedure was followed for several concentrations, C, of $Ru(NH_3)_6^{3+}$ in solution, and the data are presented in the form of a plot of log Γ_{Ru} vs. log C in Figure 4.2. The plot shows a region at low loading in which incorporation is linear with the concentration in solution. Above about 5 X 10^{-6} M $Ru(NH_3)_6^{3+}$ there is significant curvature in the plot, indicating that the incorporation is increasingly difficult as the fraction of $-SO_3^-$ groups on the polymer neutralized by $Ru(NH_3)_6^{3+}$ increases.

Double potential step chronocoulometry was used to obtain values of the chronocoulometric slope, S_{Ru} in coulomb cm^{-2} $s^{-\frac{1}{2}}$, for the reduction of $Ru(NH_3)_6^{3+}$ as a function of the amount of the complex in the film (see Chapter III for a description of the technique). This slope should be proportional to Γ and to the square root of the diffusion coefficient[6] as shown in equation (4.1)

$$S = \frac{2nFD_{Ru}^{\frac{1}{2}}\Gamma_{Ru}}{\pi^{\frac{1}{2}}\Phi} \qquad (4.1)$$

Figure 4.1 Cyclic voltammogram for $Ru(NH_3)_6^{3+}$ incorporated in a Nafion film on a BPG electrode. The concentration of $Ru(NH_3)_6^{3+}$ in solution is 12 X 10^{-6} M. The surface coverage of $Ru(NH_3)_6^{3+}$ is 8.9 X 10^{-9} mole cm^{-2}. Supporting electrolyte: 0.5 M H_2SO_4. Scan rate: 5 mV s^{-1}.

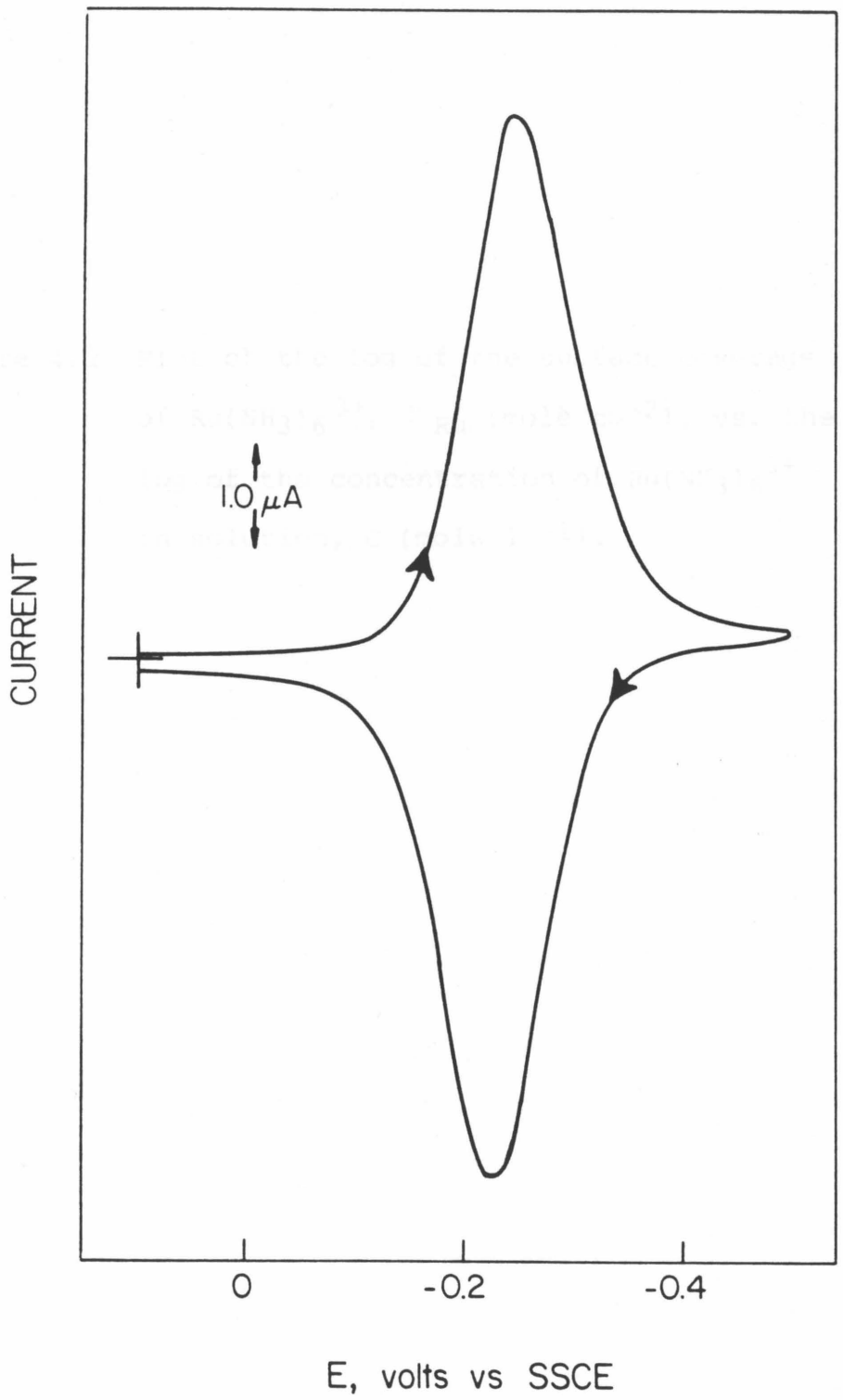
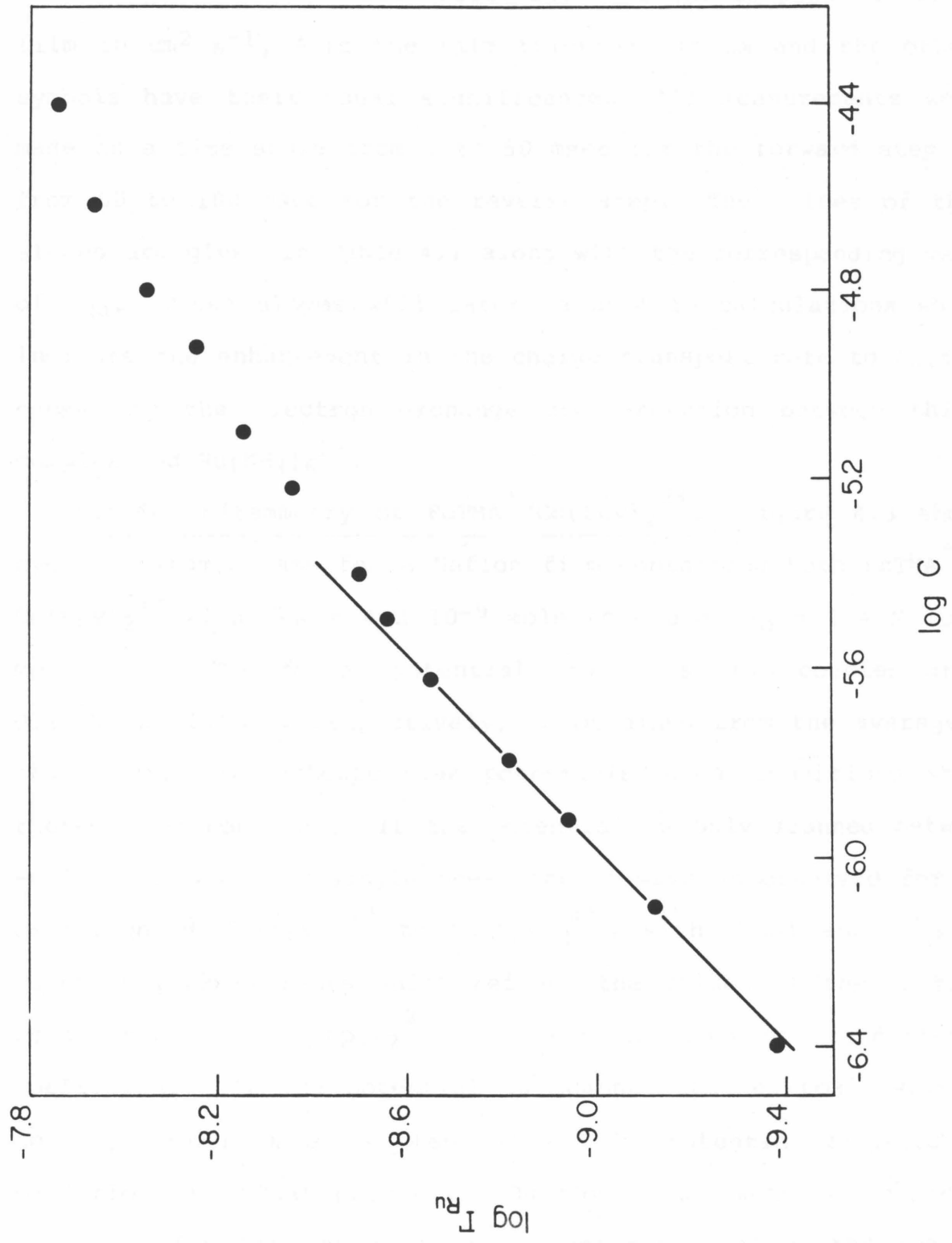

CURRENT
1.0 μA
0
-0.2
-0.4
E, volts vs SSCE

Figure 4.2 Plot of the log of the surface coverage of $Ru(NH_3)_6^{3+}$, Γ_{Ru} (mole cm^{-2}), vs. the log of the concentration of $Ru(NH_3)_6^{3+}$ in solution, C (mole l^{-1}).


-7.8
-8.2
-8.6
-9.0
-9.4
log Γ_{R_2}
-6.4
-6.0
-5.6
-5.2
-4.8
-4.4
log C

where D_{Ru} is the diffusion coefficient of the complex within the film in $cm^2\ s^{-1}$, Φ is the film thickness in cm and the other symbols have their usual significance. All measurements were made on a time scale from 0 to 50 msec for the forward step and from 50 to 100 msec for the reverse step. The values of the slopes are given in Table 4.1 along with the corresponding values of Γ_{Ru}. These slopes will later be used in calculations which indicate the enhancement in the charge transport rate to $Co(tpy)_2^{3+}$ caused by the electron exchange cross-reaction between this complex and $Ru(NH_3)_6^{2+}$.

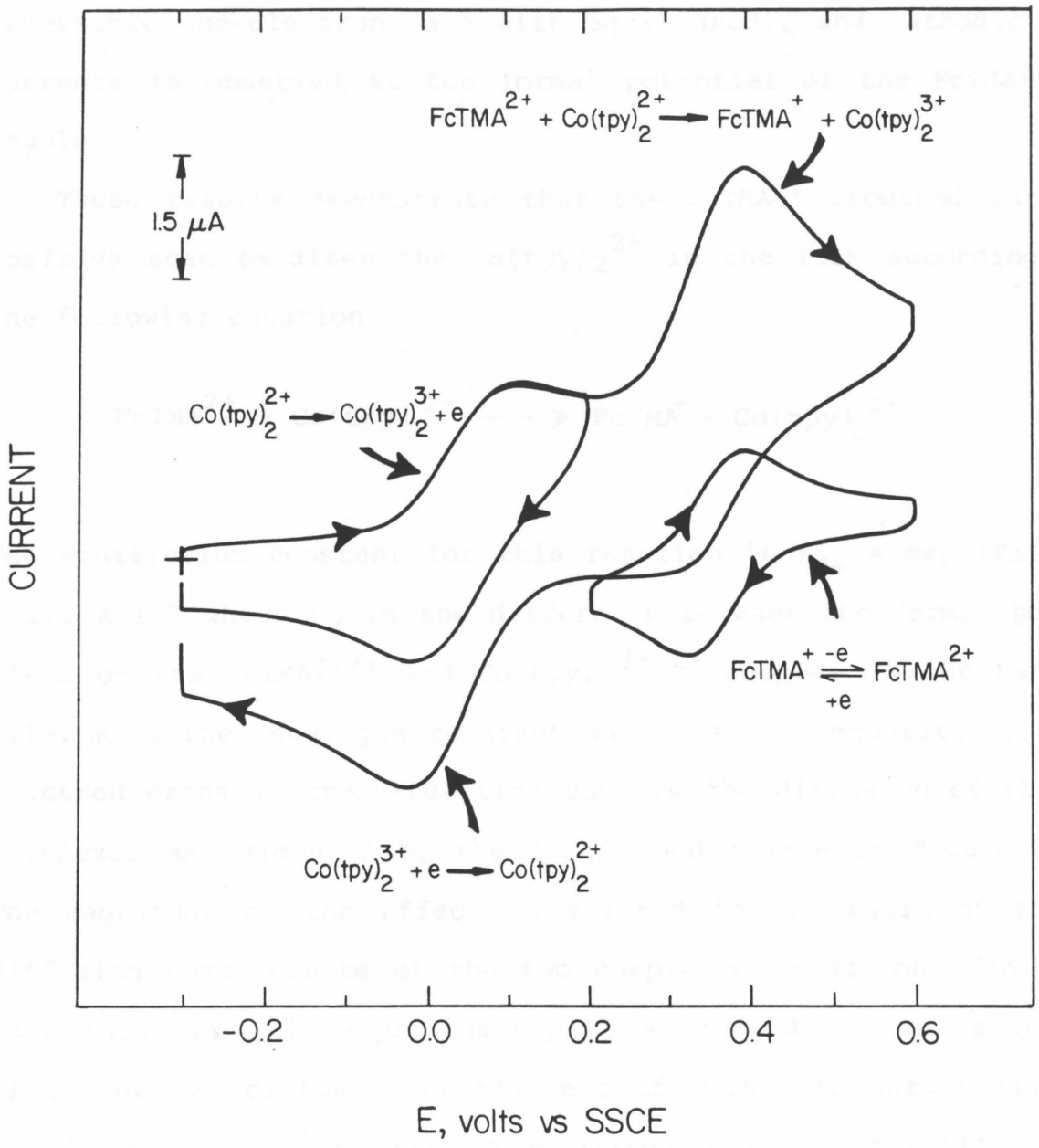
Cyclic Voltammetry of $FcTMA^+/Co(tpy)_2^{2+}$. Figure 4.3 shows cyclic voltammograms for a Nafion film containing both $FcTMA^+$ and $Co(tpy)_2^{2+}$ with $\Gamma_{Fe} = 4 \times 10^{-9}$ mole cm^{-2} and $\Gamma_{Co} = 1.4 \times 10^{-8}$ mole cm^{-2}. The formal potentials for these two couples are 0.35 V and 0.05 V, respectively, as obtained from the average of the anodic and cathodic peak potentials under conditions when there is no coupling. If the potential is only scanned between -0.3 V and 0.2 V, a single one-electron wave is observed for the oxidation of $Co(tpy)_2^{2+}$ to $Co(tpy)_2^{3+}$, with equal anodic and cathodic peak currents which reflect the values of the initial concentration of $Co(tpy)_2^{2+}$ and the square root of its diffusion coefficient. If the potential is scanned farther positively, a second, larger wave is observed at the potential at which oxidation of $FcTMA^+$ proceeds. On the return scan no cathodic component for this second wave is observed. Also, the return scan shows a considerably larger wave for the (unmediated) reduction of the $Co(tpy)_2^{3+}$ than was observed when the potential

TABLE 4.1

Chronocoulometric Slopes for $Ru(NH_3)_6^{3+}$ in Nafion.

$10^9\Gamma_{Ru}$ (mole cm^{-2})	S_{Ru} (μcoul $cm^{-2}s^{-\frac{1}{2}}$)
0.76	4.5
3.15	17
5.44	38
8.90	70
13.9	140

Figure 4.3 Cyclic voltammetry of a Nafion film containing $Co(tpy)_2^{2+}$ and $FcTMA^+$ incorporated from a solution containing these complexes at concentrations of 0.8×10^{-6} M and 1.6×10^{-6} M, respectively. Supporting electrolyte: 0.5 M Na_2SO_4. Scan rate: 50 mV S^{-1}.


FcTMA2+ + Co(tpy)2 2+ → FcTMA+ + Co(tpy)2 3+
1.5 μA
Co(tpy)2 2+ → Co(tpy)2 3+ + e
FcTMA+ -e ⇌ FcTMA2+
+e
Co(tpy)2 3+ + e → Co(tpy)2 2+
CURRENT
-0.2
0.0
0.2
0.4
0.6
E, volts vs SSCE

scan was restricted between -0.3 V and 0.2 V. If the potential is continuously cycled between 0.2 V and 0.6 V, a single, reversible one-electron wave with equal anodic and cathodic peak currents is observed at the formal potential of the $FcTMA^{2+/+}$ couple.

These results demonstrate that the $FcTMA^{2+}$ produced in the positive scan oxidizes the $Co(tpy)_2^{2+}$ in the film according to the following equation

$$FcTMA^{2+} + Co(tpy)_2^{2+} \longrightarrow FcTMA^{+} + Co(tpy)_2^{3+} \qquad (4.2)$$

The equilibrium constant for this reaction is $K_{ex} = \exp(F\Delta E/RT) = 1.2 \times 10^5$ where ΔE is the difference between the formal potentials of the $FcTMA^{2+/+}$ and $Co(tpy)_2^{3+/2+}$ couples in the Nafion film, R is the ideal gas constant and T is the temperature. This electron exchange cross-reaction couples the diffusion of the two complexes as evidenced by the large anodic wave in Figure 4.3. The magnitude of the effect is related to the ratio of the diffusion coefficients of the two complexes in Nafion. In this case this ratio is approximately 50 as judged by the reported value for the diffusion coefficient of $FcTMA^{+}$ in Nafion (1.7×10^{-10} cm^2 s^{-1} [3]) and the value reported in Chapter III for $Co(bpy)_3^{2+}$ ($2\text{-}4 \times 10^{-12}$ cm^2 s^{-1}), assuming that $Co(tpy)_2^{2+}$ and $Co(bpy)_3^{2+}$ diffuse at approximately the same rate.

The larger peak current for the cathodic wave than for the anodic wave of the $Co(tpy)_2^{3+/2+}$ couple after scanning over the

$FcTMA^{2+/+}$ potential is an interesting consequence of the more rapid diffusion of $Co(tpy)_2^{3+}$ than of $Co(tpy)_2^{2+}$ in Nafion. This difference is observed in the present experiment because of the concentration profiles of these cobalt complexes which develop during the scan. In a normal cyclic voltammogram of a reversible redox couple the peak currents of both the forward and return scans are equal and proportional to the concentration and the square root of the diffusion coefficient of whichever half of the redox couple is initially present. The return scan does not give information about the diffusion of the other half of the redox couple. A qualitative way to rationalize this is to consider that the forward scan probes the response of a flat concentration profile of the initial species while the return scan probes the response of a concentration profile which was set up by the depletion of the initial species. The situation which prevails in Figure 4.3 is quite different. Because of the much more rapid diffusion of the $FcTMA^{2+}$ complex and because it reacts essentially irreversibly with any $Co(tpy)_2^{2+}$ it encounters, the diffusion layer for $Co(tpy)_2^{3+}$ is extended much farther from the electrode than it would be without coupling. Thus, the return scan probes the response of a very thick, essentially flat concentration profile of $Co(tpy)_2^{3+}$. Under these conditions the peak current for the cathodic wave should be proportional to the concentration of $Co(tpy)_2^{3+}$ (which should equal the initial concentration of $Co(tpy)_2^{2+}$) and the square root of the diffusion coefficient of $Co(tpy)_2^{3+}$ in Nafion. Thus, information about the

diffusion coefficients of both halves of a redox couple is obtained from a single cyclic voltammogram, a quite unusual occurrence in this type of experiment.

The more rapid diffusion of $Co(tpy)_2^{3+}$ than of $Co(tpy)_2^{2+}$ in Nafion probably reflects the stronger hydrophobic interaction of $Co(tpy)_2^{2+}$ with the fluorocarbon backbone of Nafion. This was discussed in Chapter III and also in a very recent study by Martin and Dollard.[7]

The reversible response of the $FcTMA^{2+/+}$ couple obtained after prolonged cycling between 0.2 V and 0.6 V indicates that after sufficient time the $Co(tpy)_2^{3+}$ diffusion layer has extended beyond that of the $FcTMA^{2+/+}$ couple so the response of the iron complex unperturbed by electron exchange was observed. Figure 4.4 shows cyclic voltammograms which were obtained by successively adding more $FcTMA^{+}$ to a Nafion film (by increasing its concentration in the supporting electrolyte solution) which also contained $Co(tpy)_2^{2+}$. This experiment shows that if the relative amount of $Co(tpy)_2^{2+}$ present in the $FcTMA^{2+}$ diffusion layer is small enough, then a cathodic wave may be observed for the reduction of the unreacted $FcTMA^{2+}$.

Cyclic Voltammetry and Chronocoulometry of $Ru(NH_3)_6^{3+}/Co(tpy)_2^{3+}$.

Figure 4.5 shows a cyclic voltammogram obtained on a Nafion film containing both $Ru(NH_3)_6^{3+}$ and $Co(tpy)_2^{3+}$ with $\Gamma_{Co} = 3\,\Gamma_{Ru}$. The salient features of this figure are similar to those of Figure 4.3 There is a large cathodic wave with no anodic return

Figure 4.4 Cyclic voltammetry of the same film as in Figure 4.3 and under the same conditions except that the concentration of $FcTMA^+$ in solution is (A) 1.6×10^{-6} M; (B) 3.2×10^{-6} M; and (C) 6.4×10^{-6} M.

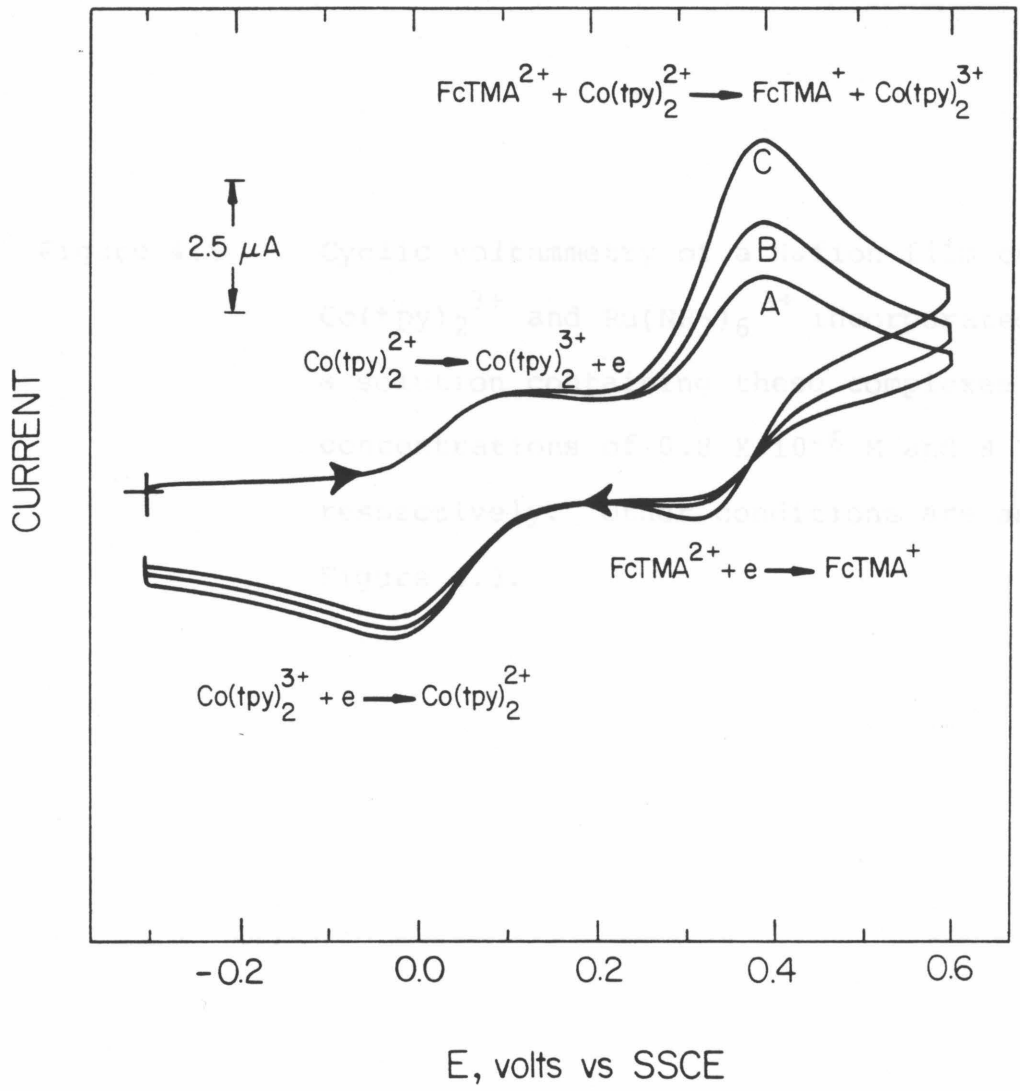
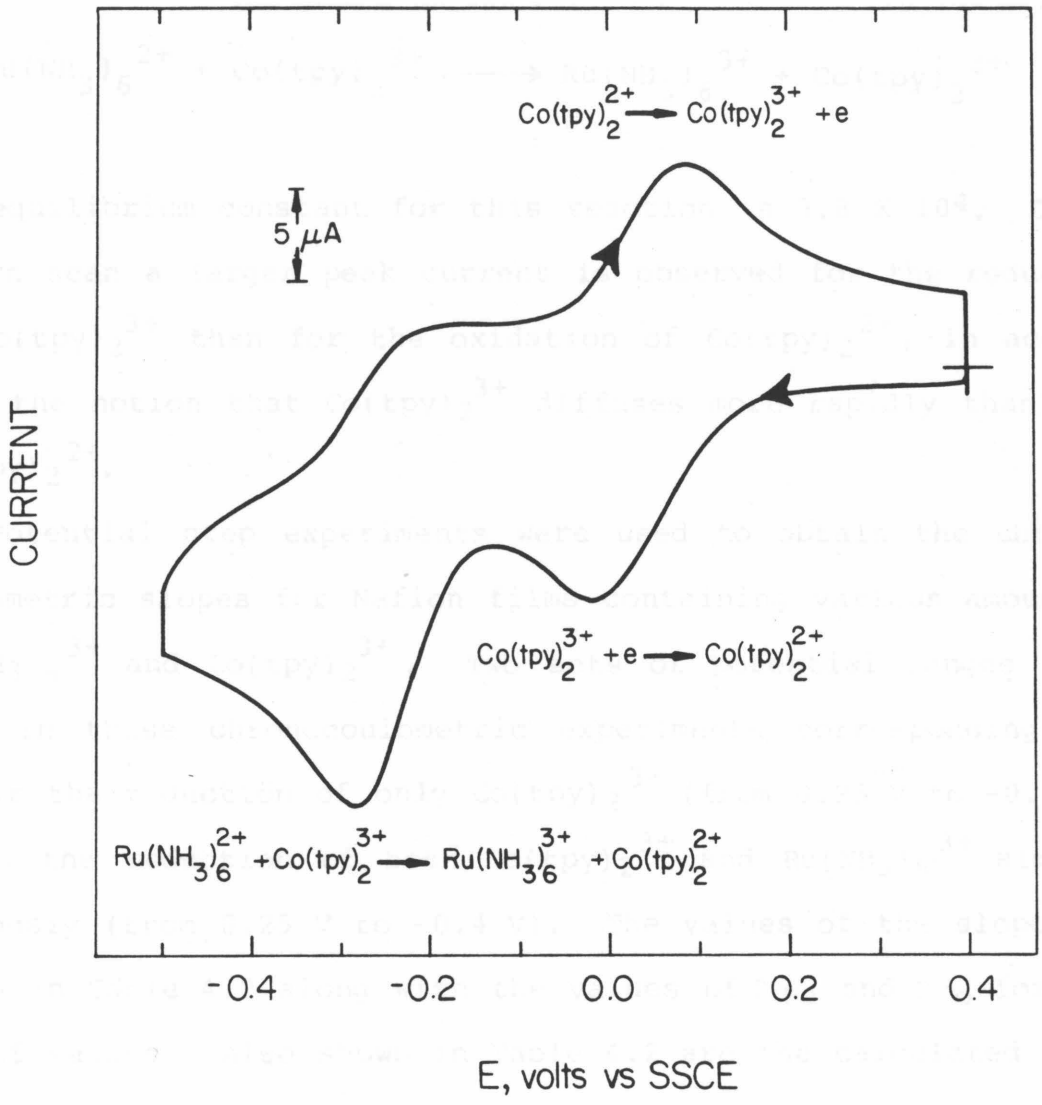

FcTMA2+ + Co(tpy)2 2+ → FcTMA+ + Co(tpy)2 3+
C
B
A
2.5 μA
Co(tpy)2 2+ → Co(tpy)2 3+ + e
FcTMA2+ + e → FcTMA+
Co(tpy)2 3+ + e → Co(tpy)2 2+
CURRENT
-0.2
0.0
0.2
0.4
0.6
E, volts vs SSCE

Figure 4.5 Cyclic voltammetry of a Nafion film containing $Co(tpy)_2^{3+}$ and $Ru(NH_3)_6^{3+}$ incorporated from a solution containing these complexes at concentrations of 0.8×10^{-6} M and 8×10^{-6} M, respectively. Other conditions are as in Figure 4.3.


Co(tpy)$_2^{2+}$ → Co(tpy)$_2^{3+}$ + e
5 μA
CURRENT
Co(tpy)$_2^{3+}$ + e → Co(tpy)$_2^{2+}$
Ru(NH$_3$)$_6^{2+}$ + Co(tpy)$_2^{3+}$ → Ru(NH$_3$)$_6^{3+}$ + Co(tpy)$_2^{2+}$
-0.4
-0.2
0.0
0.2
0.4
E, volts vs SSCE

wave at the $Ru(NH_3)_6^{3+/2+}$ formal potential. The lack of a return wave is caused by the consumption of $Ru(NH_3)_6^{2+}$ by reaction with $Co(tpy)_2^{3+}$ according to the following equation

$$Ru(NH_3)_6^{2+} + Co(tpy)_2^{3+} \longrightarrow Ru(NH_3)_6^{3+} + Co(tpy)_2^{2+} \qquad (4.3)$$

The equilibrium constant for this reaction is 9.8×10^4. On the return scan a larger peak current is observed for the reduction of $Co(tpy)_2^{3+}$ than for the oxidation of $Co(tpy)_2^{2+}$, in accord with the notion that $Co(tpy)_2^{3+}$ diffuses more rapidly than does $Co(tpy)_2^{2+}$.

Potential step experiments were used to obtain the chronocoulometric slopes for Nafion films containing various amounts of $Ru(NH_3)_6^{3+}$ and $Co(tpy)_2^{3+}$. Two sets of potential ranges were used in these chronocoulometric experiments corresponding to either the reduction of only $Co(tpy)_2^{3+}$ (from 0.25 V to -0.125 V) or to the reduction of both $Co(tpy)_2^{3+}$ and $Ru(NH_3)_6^{3+}$ simultaneously (from 0.25 V to -0.4 V). The values of the slopes are given in Table 4.2 along with the values of Γ_{Ru} and Γ_{Co} for each set of values. Also shown in Table 4.2 are the calculated values of what the chronocoulometric slopes would have been for potential steps over the $Ru(NH_3)_6^{3+/2+}$ wave in a Nafion film containing only this complex in the amounts given. It is clear that the sum of the calculated slope for $Ru(NH_3)_6^{3+}$ and the experimental slope for $Co(tpy)_2^{3+}$ is much smaller than the slope which is observed when these complexes are simultaneously

TABLE 4.2

Chronocoulometric Slopes for $Ru(NH_3)_6^{3+}$ and $Co(tpy)_2^{3+}$ in Nafion.

$10^9 \Gamma_{Ru}$ (mole cm^{-2})	$Slope_{Ru}$ [a] ($\mu coul\ cm^{-2} s^{-1/2}$)	$10^8 \Gamma_{Co}$ (mole cm^{-2})	$Slope_{Co}$ [b] ($\mu coul\ cm^{-2} s^{-1/2}$)	$Slope_{Ru+Co}$ [b] ($\mu coul\ cm^{-2} s^{-1/2}$)
0.35	2.1	1.9	30	109
1.4	7.9	2.0	40	163
2.0	11	1.6	44	207
2.7	15	3.2	89	272
4.4	28	3.0	94	348

a. Chronocoulometric slope calculated from Γ_{Ru} and the data in Table 4.1.

b. Chronocoulometric slope measured experimentally.

reduced. This comparison gives a more quantitative measure of the degree of enhancement of the charge transport rate resulting from the cross-reaction between $Ru(NH_3)_6^{2+}$ and $Co(tpy)_2^{3+}$.

DISCUSSION

The results shown in Figure 4.3 clearly demonstrate that the rate of oxidation of $Co(tpy)_2^{2+}$ in the Nafion film is enhanced by the electron exchange cross-reaction which occurs between this complex and $FcTMA^{2+}$. The same is also true for the reduction of $Co(tpy)_2^{3+}$ by $Ru(NH_3)_6^{2+}$ as shown in Figure 4.5. The magnitude of the enhancement produced by these cross-reactions is a reflection of the much more rapid diffusion rates of the two mediator complexes, $FcTMA^{2+}$ and $Ru(NH_3)_6^{2+}$, compared to the diffusion rates of either $Co(tpy)_2^{2+}$ or $Co(tpy)_2^{3+}$.

The larger cyclic voltammetric peak currents for the reduction of $Co(tpy)_2^{3+}$ than for the oxidation of $Co(tpy)_2^{2+}$ shown in Figures 4.3 and 4.5 result directly from the more rapid diffusion of $Co(tpy)_2^{3+}$ than $Co(tpy)_2^{2+}$ in these Nafion films. However, this difference in diffusion rates is only observed because of the ability of $Ru(NH_3)_6^{2+}$ and $FcTMA^{2+}$ to extend the diffusion layers of $Co(tpy)_2^{3+}$ and $Co(tpy)_2^{2+}$, respectively. Thus, the concentration profiles which define the current response of the return scans in Figures 4.3 and 4.5 are not those of a normal cyclic voltammetric experiment.

The data presented in Table 4.2 allow a quantitative assessment of the enhancement afforded by the cross-reaction between $Ru(NH_3)_6^{2+}$ and $Co(tpy)_2^{3+}$. They show that under the experimental conditions employed the currents are larger by approximately a factor of three than those which would have obtained in the

absence of coupling. The degree of the enhancement may be controlled by varying the ratio of the concentrations of the two diffusing species.

In this way the currents obtained from a film containing a given pair of complexes (such as $Ru(NH_3)_6^{3+}/Co(tpy)_2^{3+}$ or $FcTMA^{+}/Co(tpy)_2^{2+}$), each with its own characteristic diffusion coefficient, may be optimized.

CONCLUSION

An important message from this work is that the presence of a relatively small amount of a rapidly diffusing mediator can greatly accelerate the rate of charge transport to a more sluggish species in a polymer film. This effect should occur in any medium, however the large range of diffusion coefficients observed for different species in polymer films makes them the ideal choice for observing such coupling.

The large enhancement in current available through the use of charge transport mediators has important implications in the development of electrocatalytic applications of polymer modified electrodes. By taking advantage of diffusional coupling, it should no longer be necessary to demand that a catalyst have both rapid diffusion rates in the polymer film and rapid catalytic rates. In fact, because both of these characteristics are seldom found in a given catalyst, the use of charge transport mediators may serve to greatly expand the list of practical electrocatalysts suitable for use in polymer modified electrodes. The next chapter describes an electrocatalytic system based on these ideas.

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CHAPTER V

Catalysis of the Electroreduction of Dioxygen by Cobalt Tetraphenylporphyrin Incorporated in a Nafion Film

INTRODUCTION

Much of the current interest in polymer modified electrodes centers around their possible uses in electrocatalysis. The appeal of these electrodes results from their ability to confine many monolayers of a catalyst to the electrode surface. This increases the number of collisions between the catalyst and the substrate (relative to monolayer coverage), thereby increasing the probability of reaction. While the actual number of electrocatalytic applications of such electrodes is rather small,[1-6] there has been significant progress in the understanding of the different processes which may control the current in such applications.[1,3b,4,6-9] Three important limiting cases emerge from these treatments. In the first case, the rate limiting process is the transport of the substrate through the polymer film so that it may encounter the catalyst. In the second, the transport of electrons from the electrode to the catalyst sites (or vice versa) in the film is rate limiting. In the third, the rate limiting process is the chemical reaction between the catalyst and the substrate. In order to take advantage of the high reactivity of some catalysts it is desirable that slow

transport processes should never limit the catalytic current, but rather that the intrinsic rate of the reaction between the catalyst and the substrate should be expressed. Thus, one requires both that the catalyst be highly reactive with the chosen substrate and that it support high charge transport rates through the polymer film. This second requirement may be fulfilled by catalysts which have either rapid molecular diffusion in the polymer film or high self-exchange rates so they may take advantage of the electron hopping mechanism for charge transport which is seen for some redox species in polymer films[10,11] (see Chapter III). However, neither of these characteristics is likely to be ubiquitous in practical electrocatalysts for the following reasons. Rapid molecular diffusion usually results from an absence of strong interactions between the catalyst and the film,[12] implying the possibility of rapid loss of the catalyst. On the other hand, high self-exchange rates are generally only observed for redox couples which do not experience significant ligation changes accompanying the redox event,[13] a property unlikely to be common to a wide variety of catalysts.

An approach to the solution of this problem is to find simple, reliable ways of immobilizing catalysts in the films and then to provide an ancillary method of transporting charge from the electrode to the catalyst sites. The present study demonstrates just such an approach. Tetraphenylporphyrin, H_2TPP, is stably incorporated into either Nafion films on graphite

electrodes or free standing Nafion membranes. Spectral measurements on the Nafion membranes confirm the incorporation and the subsequent insertion of cobalt into the porphyrin to give CoTPP. The electroreduction of dioxygen is then accomplished with the CoTPP/Nafion films on graphite electrodes using CoTPP as the catalyst and $Ru(NH_3)_6^{3+}$, co-incorporated into the Nafion film, as an electron mediator which serves to deliver electrons from the electrode to the immobilized catalyst sites. Variation of the amount of $Ru(NH_3)_6^{3+}$ in the film allows control of the charge transport rate to the catalyst. The experimental results are in qualitative agreement with a theoretical description of such systems derived by Saveant and co-workers.[9] Using this theory an estimation of the rate constant for the catalytic reaction is obtained.

EXPERIMENTAL

Materials and Instrumentation. The Nafion coating solution was described in Chapter IV. A 1200 equivalent weight Nafion membrane (supplied as a sample by E. I. du Pont de Nemours Co.) was used for the spectral measurements on the incorporation and metallation of meso-tetraphenylporphyrin, H_2TPP. $Ru(NH_3)_6Cl_3$ (Matthey Bishop, Inc.), H_2TPP (Strem Chemicals, Inc.) and $Co(NO_3)_2$ (Allied Chemical Corp.) were used as received. Supporting electrolyte solutions, 0.5 M in either H_2SO_4 (Mallinckrodt, Inc.) or Na_2SO_4 (Allied Chemical Corp.), were prepared using deionized water after passage through a Barnstead Nanopure purification train. Basal plane graphite (BPG) electrodes were prepared as described in Chapter III. A calomel electrode saturated with sodium chloride (SSCE) was used in all experiments. Standard two-compartment cells were used in the cyclic voltammetric and rotating disk electrode experiments.

The instrumentation was described in Chapter III, except for the following. Rotating disk voltammetry was done with a Pine Instrument Co. RDE 3 bipotentiostat and an ASR 2 rotator with an ASR speed control. A Hewlett-Packard Model 8450 A spectrophotometer was used to obtain the visible spectra of the porphyrins after their incorporation into the Nafion membranes. Spectra of the membranes were obtained by clamping them between two microscope slides in a locally constructed sample holder.

Procedures. The Nafion membrane was cleaned before use by soaking in isopropanol for several hours. This removed most of a yellow-brown impurity which was initially present. The membranes were soaked for several days in a 50% H_2SO_4 aqueous solution saturated with the green, doubly-protonated form of meso-tetraphenylporphyrin, H_4TPP^{2+}, to allow for its incorporation. Cobalt was inserted into the incorporated porphyrin by immersing the membrane in a 0.1 M aqueous solution of $Co(NO_3)_2$ and heating at 80° C for two hours. After cooling, the excess unreacted cobalt was driven from the membrane by stirring it in 0.25 M NaCl.

Nafion films were prepared by casting microliter aliquots of the 0.52 wt. % solution onto BPG rotating disk electrodes of area 0.174 cm^2 and allowing the solvent to evaporate. Films were made using 8 μl aliquots unless otherwise specified. Because of the long soaking times required in strongly acidic solutions for the incorporation of the H_4TPP^{2+} into the Nafion films (typically 2-3 days), special care was required in the preparation of the electrodes. Cylinders of the BPG electrode material approximately 1 cm long were mounted on the end of a rotating disk electrode shaft using heat-shrinkable polyolefin tubing.[14] After cleaving the end of the electrode with a razor blade to expose a fresh surface of graphite, the electrode was subjected to moderate heat from a heat gun. The electrode was heated enough to cause the tubing to become quite soft, thereby forming a very tight seal around the exposed end of the electrode. If this procedure was

not followed very large background currents were observed, presumably because of creeping of the acid solution between the electrode material and the tubing.

Incorporation of H_4TPP^{2+} into the Nafion films was done using the same method as for the Nafion membranes. This procedure gave a lime green color to the surface of the electrodes, with the color being much more intense than that of the much thicker Nafion membrane. Thus, the film incorporates much larger quantities of H_4TPP^{2+} than does the membrane, indicating a more open structure for the film than for the membrane, as observed in Chapter II.

Metallation was also accomplished using the same method as that used with the membranes. After this procedure, the electrodes had a brown-purple color characteristic of CoTPP. No evidence of the green H_4TPP^{2+} was observed even when the film was briefly contacted with acidic solutions, indicating complete and stable metallation. The quantity of electroactive CoTPP (i.e. the quantity available for reaction with electron mediators) in a given film was obtained as described in the Results section.

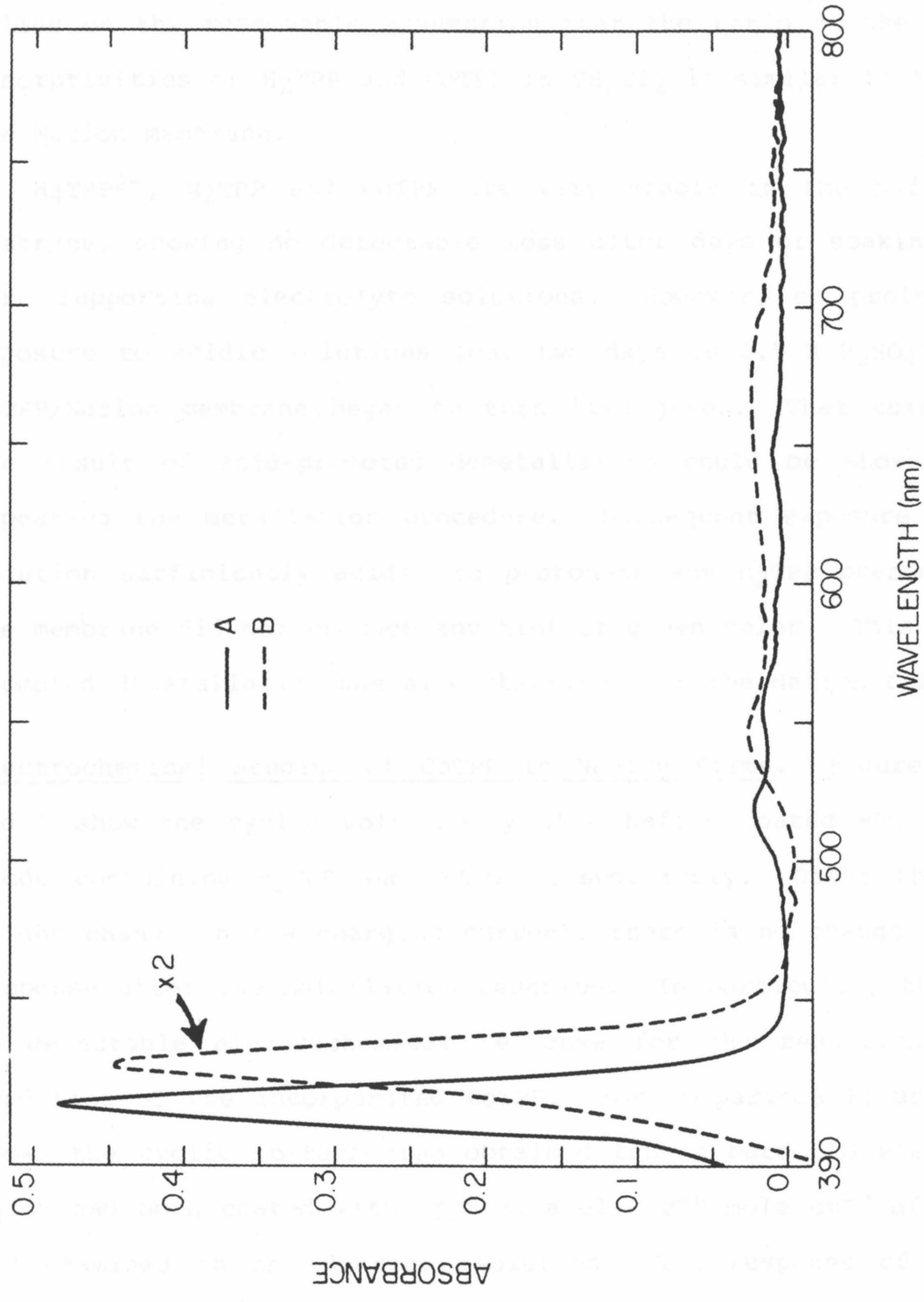
RESULTS

Spectra of Porphyrins in Nafion Membranes. As described in the Experimental section a Nafion membrane was immersed in a 50% H_2SO_4 aqueous solution saturated with H_4TPP^{2+} to incorporate the green porphyrin dication. After the incorporation the membrane was soaked in a pH 10 borate buffer solution to deprotonate the green dication to give the brown-purple neutral porphyrin. This change in the color of the membrane required approximately 3-5 minutes and was quite reversible by soaking alternatively in 0.5 M H_2SO_4 and pH 10 buffer.

Figure 5.1A shows a spectrum of the neutral H_2TPP incorporated in a 1200 eq. wt. Nafion membrane. The positions and relative intensities of the Soret (412 nm) and Q bands (515, 553, 592 and 650 nm) are in very good agreement with the reported spectrum of H_2TPP in CH_2Cl_2,[15] indicating that H_2TPP has been incorporated and remains intact. Figure 5.1B shows a spectrum of the same membrane after metallation of the porphyrin with $Co(NO_3)_2$. Comparison of the positions and relative intensities of the Soret (426 nm) and Q bands (542 nm) with literature data[16] is convincing evidence for the successful insertion of cobalt into the porphyrin. A rough comparison of the absorbances of the Soret bands of H_2TPP and CoTPP shown in Figure 5.1, using the fact that the molar absorptivity of H_2TPP[15] in CH_2Cl_2 is about twice that of CoTPP[16] in CH_2Cl_2, reveals that there is little loss of porphyrin during the metallation reaction. Thus, this

Figure 5.1 (A) Absorption spectrum of H_2TPP incorporated in a 1200 eq. wt. Nafion membrane.

(B) Absorption spectrum of CoTPP produced by metallation of H_2TPP in the same membrane. Note that the sensitivity is doubled for this spectrum.


ABSORBANCE
0.5
0.4
0.3
0.2
0.1
0
390
500
600
700
800
WAVELENGTH (nm)
A
B
x2

reaction proceeds in high yield in the membrane. This conclusion relies on the reasonable assumption that the ratio of the molar absorptivities of H_2TPP and CoTPP in CH_2Cl_2 is similar to that in the Nafion membrane.

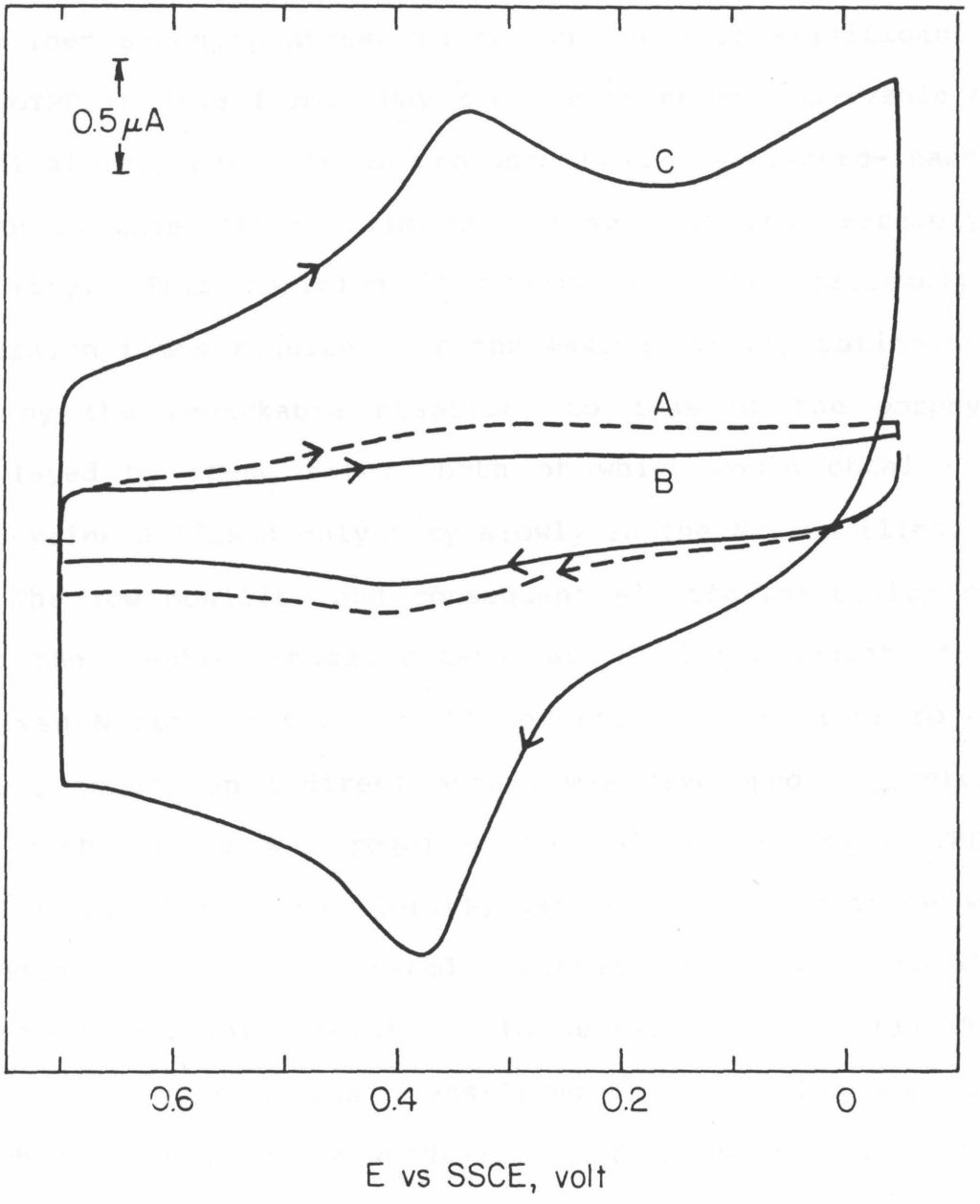
H_4TPP^{2+}, H_2TPP and CoTPP are very stable in the Nafion membrane, showing no detectable loss after days of soaking in pure supporting electrolyte solutions. However, on prolonged exposure to acidic solutions (ca. two days in 0.5 M H_2SO_4) the CoTPP/Nafion membrane began to turn lime green. That this was the result of acid-promoted demetallation could be shown by repeating the metallation procedure. Subsequent exposure to a solution sufficiently acidic to protonate any H_2TPP present in the membrane did not produce any hint of green color. This acid-promoted demetallation was also observed with the Nafion films.

Electrochemical Studies of CoTPP in Nafion Films. Figure 5.2A and B show the cyclic voltammetry of a Nafion coated BPG electrode containing H_2TPP and CoTPP, respectively. Other than a slight change in the charging current, there is no change in the response after the metallation reaction. In particular, there is no detectable electrochemical response for the reduction or oxidation of the incorporated CoTPP. For comparison Figure 5.2C shows the cyclic voltammogram obtained from a bare BPG electrode which had been coated with approximately 10^{-8} mole cm^{-2} of CoTPP and examined in an identical solution. The response of the Co(III)/Co(II) redox couple is clearly seen at 0.35 V.

Figure 5.2 (A) Cyclic Voltammetry of a BPG electrode coated with a Nafion film containing H_2TPP.

(B) Cyclic voltammetry of the same film as in (A) after insertion of cobalt into the porphyrin to make CoTPP.

(C) Cyclic voltammogram of a BPG electrode with ca. 10^{-8} mole cm^{-2} of CoTPP adsorbed on its surface. Scan rate: 50 mV S^{-1}. Supporting electrolyte: argon-saturated 0.5 M H_2SO_4.


0.5 μA
C
A
B
0.6
0.4
0.2
0
E vs SSCE, volt

The spectral measurements on CoTPP in the Nafion membranes previously described and the catalytic dioxygen reduction to be described strongly attest to the presence of significant amounts of CoTPP in this film. Why then is there no observable electrochemical response? It is proposed that the electro-inactivity of CoTPP in this Nafion film is a result of its extremely low mobility. This position is supported by the extremely long immersion times required for the maximum incorporation of H_4TPP^{2+} and by the remarkable stability to loss of the porphyrins displayed by these films, both of which would obtain if the porphyrins diffused only very slowly in the Nafion films.

The low mobility and consequent electro-inactivity of CoTPP made the electrochemical determination of the amount of CoTPP in a given Nafion film especially difficult. In order to overcome this problem, an indirect method was developed for determining how much charge was required to reduce the Co(III)TPP to Co(II)TPP. First, the Co(TPP)/Nafion coated electrode was left standing in an air-saturated solution for two days to allow all of the incorporated porphyrin to be oxidized to Co(III)TPP.[17,21] Then the electrode was transferred to a 0.5 M H_2SO_4 solution which contained 10^{-7} M $Ru(NH_3)_6{}^{3+}$. This complex entered the film by virtue of an ion-exchange interaction with the sulfonate groups on the polymer side chains as described in previous chapters. After thoroughly purging the solution with purified argon, a cyclic voltammogram of the $Ru(NH_3)_6{}^{3+/2+}$ couple was obtained at

a very low scan rate (5 mV s^{-1}). As shown in Chapter IV, under these conditions the film responds as a thin-layer system so that the integral of the cathodic wave gives the total quantity of material in the film which is reducible in this potential range. In this case this integral gives the sum of the surface coverages of $Ru(NH_3)_6^{3+}$ and Co(III)TPP in the film. The charge corresponding to exhaustive reduction of both of these complexes is harvested because the $Ru(NH_3)_6^{2+}$ produced at the electrode will diffuse through the film and reduce any Co(III)TPP which is present until both complexes have been completely reduced. The reduction of Co(III)TPP by $Ru(NH_3)_6^{2+}$ is thermodynamically favored by approximately 0.6 V so that the reaction should proceed essentially to completion. On the return scan the oxidation of $Ru(NH_3)_6^{2+}$ should occur unperturbed by the presence of Co(II)TPP. Thus, the integral of this anodic wave gives the total quantity of the ruthenium complex in the film. The total quantity of electrochemically harvestable CoTPP is then obtained from the difference between the integrals of the forward and return waves.

Using this procedure values for the amount of "electroactive" CoTPP incorporated in films cast from 12 X 10^{-6} l of the 0.52 wt. % Nafion coating solution were obtained which ranged between 2 X 10^{-10} and 10 X 10^{-10} mole cm^{-2}. Such a wide range was obtained because it was difficult to accurately control the degree of incorporation of H_4TPP^{2+} from the strong acid solutions. Similar values were obtained using potential step coulometry, however the

slow cyclic voltammetric method is preferable because it allows for visual correction of the background response.

Reduction of Dioxygen with CoTPP. Rotating disk voltammetry[18] was used to examine the catalytic reduction of dioxygen by the CoTPP incorporated in the Nafion films. In this technique a disk electrode is rotated about an axis through its center and normal to its surface. The rotation rate, ω, ranges between 100 and 10,000 revolutions per minute (RPM). The rotation of the electrode causes convective flow of the solution containing the species of interest toward the electrode surface. By varying the rotation rate one may control the mass transport of this species to the electrode surface.

In a typical rotating disk experiment at a bare electrode the electrode is rotated with a constant radial velocity while the electrode potential is slowly scanned through the chosen potential range. The current rises near the potential for the redox process of interest and finally reaches a plateau value after this potential, giving a sigmoidally shaped current-potential curve. When the redox process is kinetically facile the value of the limiting current, i_{lim}, on the plateau is given by the Levich equation[19]

$$i_{Lev} = 4.80\ nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C \qquad (5.1)$$

where i_{Lev} is the Levich current (amp) which in this case is

equal to the limiting current, n is the number of electrons consumed in the redox process, F is the Faraday constant, A is the electrode area (cm^2), D and C are the diffusion coefficient ($cm^2\ s^{-1}$) and concentration (mole cm^{-3}), respectively, of the redox species, ω is the rotation rate (RPM) and ν is the kinematic viscosity of the solvent ($cm^2\ s^{-1}$).

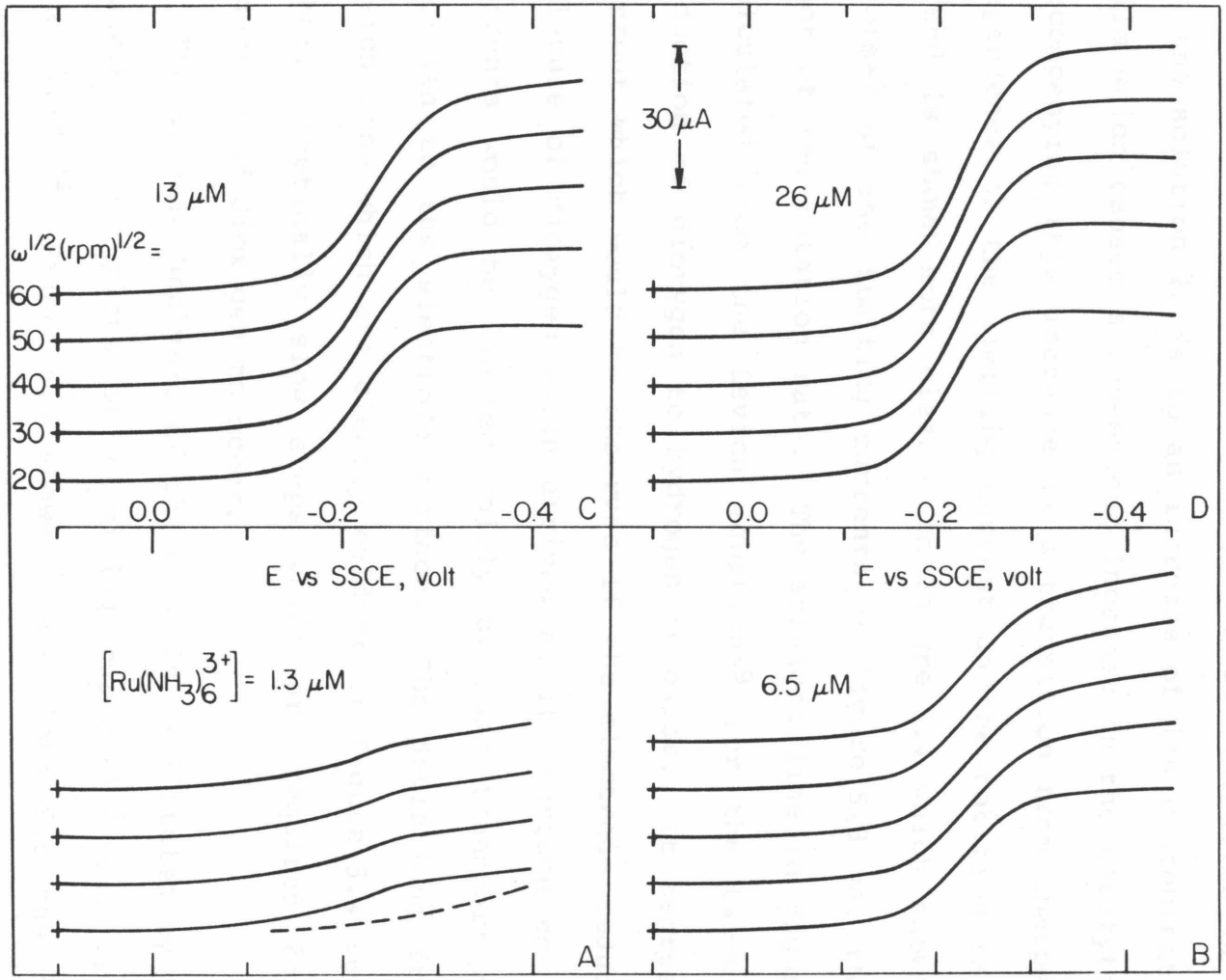
When a Nafion film containing CoTPP is prepared on a rotating disk electrode and examined for potency as a dioxygen reduction catalyst a moderate reduction current (ca. 30 to 40 μamp cm^{-2} at a rotation rate of 400 RPM) is observed on the first scan. The $E_{\frac{1}{2}}$[20] for this reduction is variable from film to film with an average value of approximately -0.15 V. However, after the initial scan with a given electrode all subsequent scans show much lower currents. It should be noted here that at a bare BPG electrode to which CoTPP has been adsorbed the $E_{\frac{1}{2}}$ for the reduction of dioxygen is between 0.1 V and 0.15 V,[21] significantly more positive than the value observed here. The origins of this shift in the potential of the reduction and the loss of catalytic activity after the first scan are unclear at this time, however it is not unlikely that the extremely low mobility of the porphyrin in the Nafion film is somehow related to these observations.

In order to realize larger currents the reduction of dioxygen was examined in solutions containing micromolar concentrations of $Ru(NH_3)_6^{3+}$. This complex can enter the polymer film by ion-exchange and, at the proper potential, act as an electron

mediator between the electrode and the "immobilized" catalyst sites. Figure 5.3A shows the results of such an experiment at a rotating disk electrode in a 0.5 M H_2SO_4 solution saturated with air[22] and containing 1.3 X 10^{-6} M $Ru(NH_3)_6^{3+}$. The dashed line shows the response which is observed before the porphyrin in the film has been metallated. Only the background response of graphite is observed. No response is observed from the $Ru(NH_3)_6^{3+}$ incorporated into the film because the current sensitivity is too low to allow the detection of the small amount of this complex present in the film. There is no catalytic reduction of dioxygen at the $Ru(NH_3)_6^{3+/2+}$ formal potential (-0.24 V) because $Ru(NH_3)_6^{2+}$ is a very poor catalyst for this reaction.[23] The solid lines in Figure 5.3A show the rotation rate dependence of the current which is observed when the film contains CoTPP. The potential at which the catalytic reduction occurs is that for the reduction of $Ru(NH_3)_6^{3+}$ to $Ru(NH_3)_6^{2+}$. As previously discussed, almost no reduction current is observed at potentials at which the CoTPP catalyst would operate at a bare electrode. Instead, at potentials where $Ru(NH_3)_6^{2+}$ is produced this complex diffuses away from the electrode and reduces the CoTPP catalyst and the catalytic intermediates which result from the reactions of CoTPP with dioxygen. Thus, by mediating charge transport to the "immobilized" catalyst sites $Ru(NH_3)_6^{2+}$ allows the incorporated CoTPP to function as an effective dioxygen reduction catalyst.

As can be seen from the solid lines in Figure 5.3A, the dioxygen reduction current appears to be independent of the

Figure 5.3 (A) Rotating disk voltammetry of a BPG electrode coated with a Nafion film containing CoTPP (2.5×10^{-10} mole cm^{-2}) and $Ru(NH_3)_6^{3+}$. Scan rate: 2 mV s^{-1}. Supporting electrolyte: air-saturated 0.5 M H_2SO_4 containing 1.3×10^{-6} M $Ru(NH_3)_6Cl_3$. Rotation rates: 400, 900, 1600 and 2500 RPM from bottom to top, respectively. (B-D) The same conditions as in (A) prevail except that the concentration of $Ru(NH_3)_6Cl_3$ in solution is increased as shown. Rotation rates: 400, 900, 1600, 2500 and 3600 RPM from bottom to top, respectively.


13 μM
ω^1/2 (rpm)^1/2 =
60
50
40
30
20
0.0
-0.2
-0.4
C
30 μA
26 μM
0.0
-0.2
-0.4
D
E vs SSCE, volt
E vs SSCE, volt
[Ru(NH3)6 3+] = 1.3 μM
6.5 μM
A
B

rotation rate when the relative concentration of $Ru(NH_3)_6^{3+}$ in the solution (and therefore in the film) is low. As Figure 5.3 B-D demonstrate, increasing the concentration of $Ru(NH_3)_6^{3+}$ in the solution leads to an increase of its concentration in the film which causes a consequent increase in the catalytic current. Accompanying this increase is a transition from independence to dependence of the limiting current on the rotation rate. This trend is shown more clearly in Figure 5.4 which shows Levich plots[19] of the limiting currents in Figure 5.3 vs. the square root of the rotation rate. The straight line in Figure 5.4 is calculated from the Levich equation[19] for the two-electron reduction of dioxygen to hydrogen peroxide. It represents the current which would be observed if the electrode reduced every molecule of dioxygen which arrived at its surface so that the currents would be limited solely by mass transport of the dioxygen to the electrode surface. The deviations from this Levich line which are clearly evident in Figure 5.4 result from other, kinetically slow steps which are required for the reduction of dioxygen to occur.

The kinetic analysis of the data is facilitated by the use of Koutecky-Levich plots of $(\text{limiting current})^{-1}$ vs. $(\text{rotation rate})^{-\frac{1}{2}}$.[19,24] Figure 5.5 shows these plots for the data in Figure 5.3. The dashed line in this plot is calculated from the Levich equation for the two-electron reduction of dioxygen.

The data indicate that there are two limiting classes of behavior depending on the concentration of $Ru(NH_3)_6^{3+}$ in the

Figure 5.4 Levich plots of the limiting currents of the rotating disk voltammograms shown in Figure 5.3 vs. (rotation rate)$^{\frac{1}{2}}$. The straight line gives the calculated response for the two-electron reduction of dioxygen.

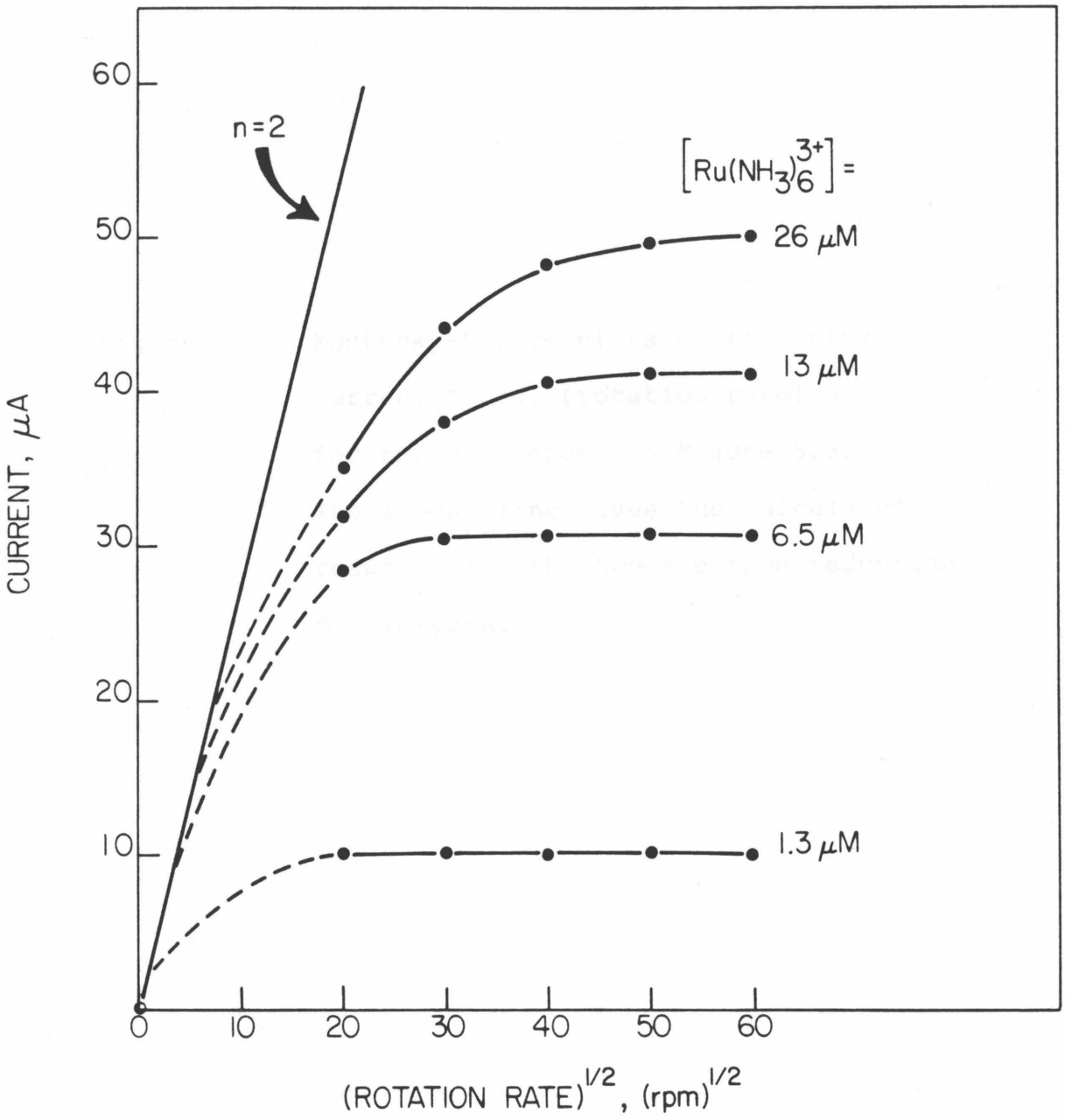
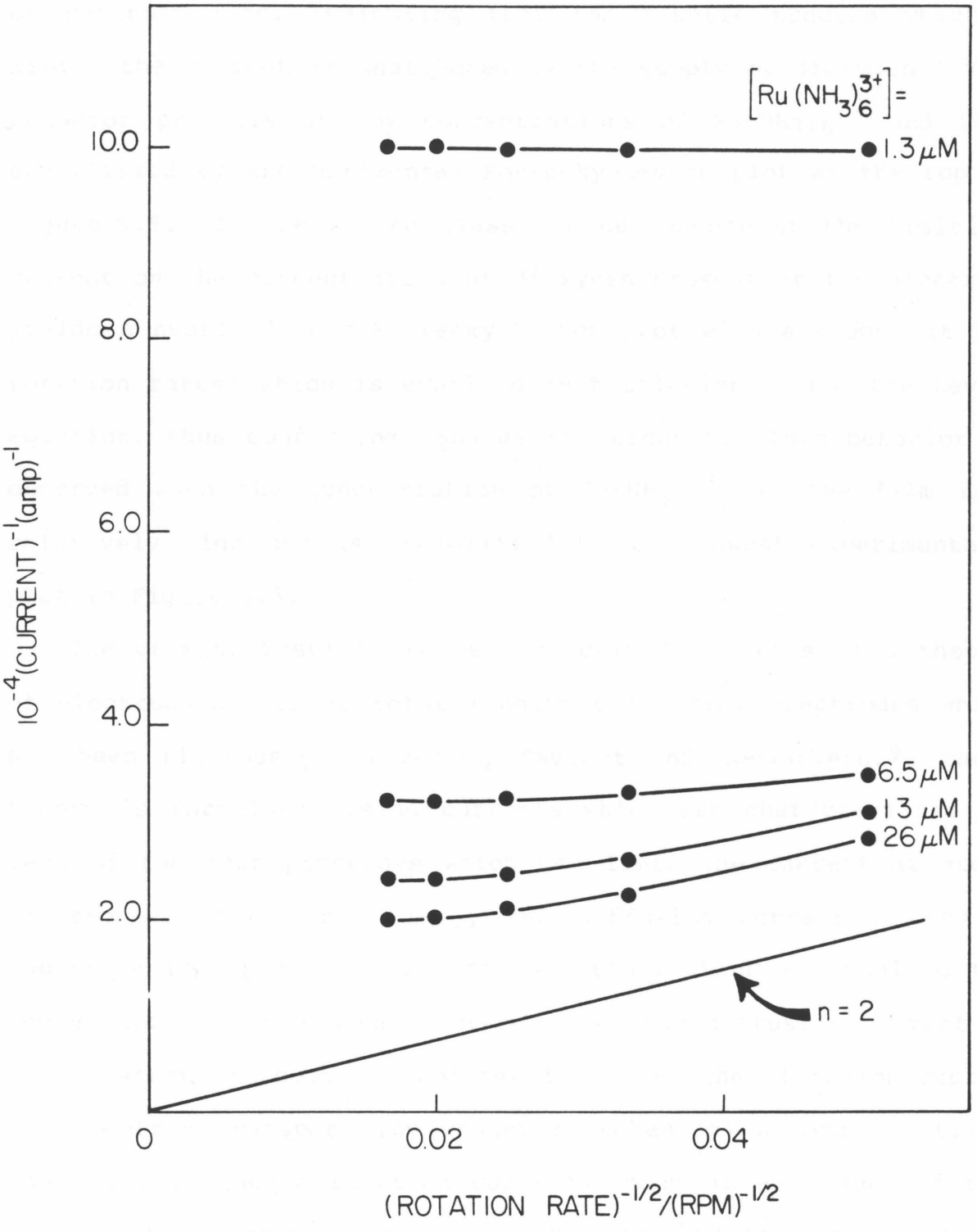

60
50
40
30
20
10
0
10
20
30
40
50
60
n=2
$[Ru(NH_3)_6^{3+}]$ =
26 μM
13 μM
6.5 μM
1.3 μM
CURRENT, μA
(ROTATION RATE)$^{1/2}$, (rpm)$^{1/2}$

Figure 5.5 Koutecky-Levich plots of (limiting current)$^{-1}$ vs. (rotation rate)$^{-\frac{1}{2}}$ for the data shown in Figure 5.3. The lowest line gives the calculated response for the two-electron reduction of dioxygen.


$\left[Ru(NH_3)_6^{3+}\right]$ =
1.3 μM
6.5 μM
13 μM
26 μM
n = 2
10.0
8.0
6.0
4.0
2.0
0
0.02
0.04
10^{-4}(CURRENT)$^{-1}$(amp)$^{-1}$
(ROTATION RATE)$^{-1/2}$/(RPM)$^{-1/2}$

film. In the first class the current appears to be independent of rotation rate, indicating that the kinetic process which limits the current is unaffected by the supply of dioxygen. This behavior prevails at low concentrations of $Ru(NH_3)_6^{3+}$ and is exemplified by the horizontal Koutecky-Levich plot at the top of Figure 5.5. In the second class the dependence of the limiting current on the concentration of dioxygen present at the electrode yields a nearly linear Koutecky-Levich plot with a slope (at low rotation rates) which is equal to that calculated from the Levich equation, thus confirming H_2O_2 as the product. This behavior is observed when the concentration of $Ru(NH_3)_6^{3+}$ in the film is relatively high and is exemplified by the lowest experimental plot in Figure 5.5.

The present results are best described in terms of a theory of electrocatalysis at rotated polymer modified electrodes which has been rigorously derived by Saveant and co-workers.[9] The theory is formulated using currents which are characteristic of each of the four processes which can limit the current at such electrodes. They are: i_{Lev}, the diffusion current of the substrate (dioxygen) through the solution, which is equal to the Levich current at a bare electrode; i_S, the diffusion current of the substrate through the polymer film; i_E, the diffusion current for electron transport (by whatever mechanism) across the film; and i_k, the kinetic reaction current, which is a measure of the rate of the catalytic reaction. This formulation suggests a scheme embodying a series of steps which must occur for the

reaction to proceed. The substrate (dioxygen) diffuses through the solution and then through the film to meet the outgoing electrons; the electrons diffuse away from the electrode and are delivered to the catalyst sites; when the substrate encounters reduced catalyst sites the catalytic reaction occurs. In order to apply the theory the relative contributions of each of these characteristic currents to the observed current must be compared. To this end, the uncatalyzed reduction of dioxygen (which proceeds at a more negative potential than the catalytic reduction) was examined both at a bare BPG electrode and at a Nafion coated BPG electrode which did not contain any porphyrin. The limiting currents at the two electrodes were identical, and were much larger than those shown in Figure 5.3. This experiment shows that the Nafion film does not present a significant barrier to the diffusion of dioxygen. Thus, i_S does not limit the observed current in the catalytic system.

The apparent independence of the limiting currents from the rotation rate at low mediator ($Ru(NH_3)_6^{3+}$) concentrations suggests that the process which limits the current depends on the concentration of the mediator and not on the concentration of dioxygen. There are two processes which fit this description. One is the transport of electrons from the electrode to the catalyst sites by $Ru(NH_3)_6^{2+}$, i_E. The other is the electron exchange between $Ru(NH_3)_6^{2+}$ and the catalytic intermediates. It is not unlikely that these processes exert mixed control over the current. However, the theory for the particular situation which

obtains under these conditions is not yet developed so the relative contributions of these two processes to the observed current cannot be determined at the present time.

By increasing the mediator concentration a situation obtains in which both i_E and i_k exert mixed control over the observed current. The theory predicts non-linear Koutecky-Levich plots for this situation,[9a] as observed in Figure 5.5 for the intermediate concentrations of $Ru(NH_3)_6^{3+}$. Further increasing the mediator concentration results in a situation in which i_E becomes large compared to i_k. In this case the observed current is no longer dependent on the electron transport diffusion current. Instead, the current depends on the intrinsic rate of the catalytic reaction. Thus, this situation is designated as the R case.[9a] This corresponds to a situation in which the concentration of $Ru(NH_3)_6^{2+}$ is relatively high and constant across the thickness of the film, and its diffusion provides a flux of electrons to the catalyst sites which is sufficient to allow the catalysis to proceed at its intrinsic rate. In the R case the reaction layer in which the catalysis occurs extends across the entire film,[9a] and all of the CoTPP in the film takes part in the catalytic reaction. The theory for the R case demands a linear Koutecky-Levich plot with the same slope as that calculated from the Levich equation.[9a] Figure 5.5 shows that there is a clear tendency toward this behavior as the concentration of $Ru(NH_3)_6^{3+}$ is increased.

The expression for the catalytic limiting current in the R case is given by equation (5.2).

$$\frac{1}{i_{lim}} = \frac{1}{i_{Lev}} + \frac{1}{i_k} \qquad (5.2)$$

The expression for i_k is given by equation (5.3)

$$i_k = 10^3\ nFAk\Gamma\kappa C \qquad (5.3)$$

where k ($M^{-1}\ s^{-1}$) is the second order rate constant governing the reaction of the catalyst with dioxygen, Γ (mole cm^{-2}) is the total quantity of catalyst on the electrode, κ is the partition coefficient for the incorporation of dioxygen into the film and the other symbols have their usual significance. The product κC gives the concentration of dioxygen in the film, which is assumed to be equal to C (i.e. $\kappa = 1$). The form of equation (5.2) suggests that the intercept of the Koutecky-Levich plot on the $(current)^{-1}$ axis should give i_k^{-1}. Thus, the evaluation of Γ as previously described allows the calculation of k.

As noted above, the theory for the R case demands a linear Koutecky-Levich plot. While the experimental data in Figure 5.5 show a tendency toward linearity at high concentrations of $Ru(NH_3)_6^{3+}$, the plot for the highest concentration is clearly not linear over the entire range of rotation rates examined. However, in order to arrive at a rough estimate of k the linear portion of this plot was extrapolated to the $(current)^{-1}$ axis to

give i_k^{-1}. The range of rate constants obtained in this way from plots for several films is (2 - 10) X 10^4 M^{-1} S^{-1}. Such a wide range was obtained because the total surface coverage of CoTPP was not obtained for every film. Instead, the largest and smallest values of this parameter were used together with the extrapolated Koutecky-Levich intercepts to calculate a range of values for k.

DISCUSSION

Perhaps the most interesting result of this work is the remarkable stability of the CoTPP catalyst in the Nafion film. The porphyrin molecule itself is quite stable in the film even under rather harsh conditions, as for example in 80° C aqueous solution or in 50% H_2SO_4 solution. The CoTPP catalyst is stable to loss from the film under the conditions for the catalysis. While prolonged exposure to strongly acidic media will induce demetallation of this catalyst, this may easily be reversed by repeating the metallation procedure.

This method of introducing lipophilic ligands into polymer films by extraction from concentrated acid solutions followed by in situ metallation may prove to be a useful route to the construction of films containing different kinds of catalysts based on various transition metals and ligands such as porphyrins, phthalocyanines and other acid-resistant molecules. It should be noted in this regard that the solubility of the ligand in the acidic loading solution may be quite low, as in the case of tetraphenylporphyrin, without significantly reducing the amount of incorporation. This is because most organic ligands are likely to have very large partition coefficients for incorporation due not only to electrostatic interactions but also to hydrophobic interactions with the polymer as discussed in previous chapters.

An advantage of this technique of film preparation is the convenience of using water-soluble metal salts in the metallation reaction. The use of water-soluble salts obviates the search for a suitable lipophilic salt of a given metal as is generally required for metal insertion reactions of lipophilic porphyrins.[25] Preliminary experiments indicate that FeTPP may be synthesized in Nafion films in much the same fashion as is CoTPP, suggesting the generality of the technique.

The use of a redox mediator such as $Ru(NH_3)_6^{3+}$ to provide for charge transport to the catalyst allows its choice to be based on its intrinsic reactivity with the substrate and not on facile electrode kinetics or a high rate of diffusion in the film. In fact, this study shows that there is an advantage in using catalysts which diffuse only very slowly within the polymer film because this significantly retards their loss to the solution.

The ability to control the flux of reducing equivalents by varying the mediator concentration without changing the catalyst loading allows a unique test of the theoretical predictions[9] for the qualitative behavior of such a system. It is seen that the experimental observations agree quite well with the predicted behavior. That the R case may be so easily reached by increasing the mediator concentration is important because, as discussed in the Introduction, it is desirable that slow transport processes should never limit the catalytic current.

The range of values of the rate constant for the reaction of CoTPP with dioxygen in the Nafion film may be compared with those

obtained by Durand and Anson[26] for the reduction of dioxygen with a slightly different cobalt porphyrin adsorbed on edge plane pyrolytic graphite electrodes. They obtained a value of approximately 10^5 M^{-1} S^{-1}. This comparison and the similarity of many other cobalt porphyrins[21,26] in their reactivity with dioxygen indicate that the incorporation of CoTPP into the Nafion film does not seriously alter its potency as a dioxygen reduction catalyst.

CONCLUSIONS

A new method for the preparation of electrodes coated with very stable Nafion films containing tetraphenylporphyrin was presented. Facile metallation of the porphyrin with $Co(NO_3)_2$ was demonstrated spectrally. Electron mediation using a rapidly diffusing, reversible redox couple allows for the catalytic reduction of dioxygen by the CoTPP. The kinetics of this reduction are discussed within the context of a theory of electrocatalysis at rotated polymer modified electrodes developed by Saveant and co-workers.[9] The qualitative predictions of this theory were found to be in good agreement with the experimental data.

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